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VOL. 15, SEC. A. JUNE, 1937 NUMBER 6

AUTOMATIC GAIN CONTROL[1]

BY E. C. JORDAN[2]

Abstract

The simple, automatic volume control circuit of radio receivers has been adapted for use in the studio amplifier of a broadcasting station to give a semi-automatic control of programs. The circuit adjustments for optimum control action were determined experimentally, and then this control action was analyzed by means of oscillograms. The effects of different time constants and degrees of control were noted, and methods for varying the latter indicated. The circuit is shown to be distortionless, except in so far as manual control of amplifier gain may be said to introduce "distortion". The control action, while not fully automatic, is complete enough to be of real assistance to the operator.

Introduction

The full volume range of music in a broadcast program is some 65 or 75 decibels. The transmission of such a large range is difficult owing to limitations imposed, on one hand, by the minimum level of the inherent noises of the system, and, on the other hand, by the maximum signal level that can be handled without distortion. Moreover, experiments have shown that under average home conditions the range between the loudest comfortable listening level and the lowest volume sufficient to overcome background noise of both the room and the receiver is about 40 decibels. For these reasons it is necessary to "control" a program, and this is one of the chief duties of a control operator. It would seem, however, that this controlling might be done, to some extent, automatically. It was the purpose of this investigation to adapt the automatic volume control circuits of radio receivers to a broadcast audio-amplifier, and then to determine the nature and efficacy of the control action so produced.

Experimental

The principle of the usual automatic volume control circuits is to rectify some of the output of the last radio-frequency stage, filter it and apply the slowly varying d-c. component to the grids of the variable-μ tubes of the previous stages. The circuit shown in Fig. 1 was developed for the audio-frequency amplifier used. The control circuit proper is shown in heavy lines and consists of the transformer Tr_1, potentiometer P_1, tube T_3, and the filter network C and R. Tube T_2 and its associated circuit are for volume indication, and, while not necessary in the functioning of the control, they are helpful in determining the extent of the action. The first tube of the amplifier, a

[1] *Manuscript received February 16, 1937.*
Contribution from the Department of Electrical Engineering, University of Alberta, Edmonton, Canada.

[2] *Graduate student, Department of Electrical Engineering, University of Alberta.*

triode, was replaced by a tetrode, T_1, of the variable-μ type. The rectifier tube, T_3, is normally biassed beyond cut-off; this prevents the flow of plate current through the resistor R, and operates the variable-μ tube T_1 under a condition of minimum bias and, hence, maximum amplification. When a signal voltage is applied to the amplifier it appears at the input of the rectifier, and a plate

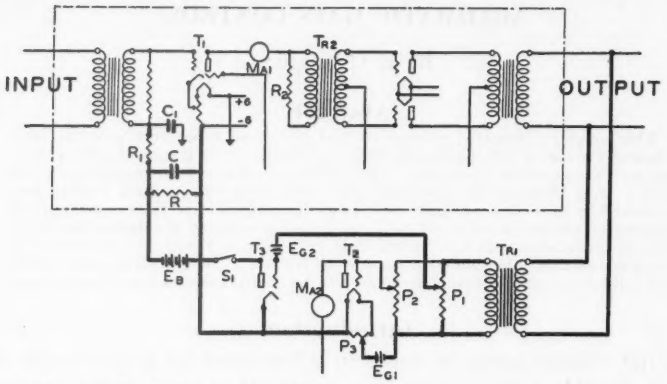


FIG. 1. *Studio broadcast-amplifier with automatic gain control circuit.*

current, whose average is proportional to the amplitude of the signal voltage flows through the circuit. This current flowing through R applies an additional bias to tube T_1. The reduction in gain is proportional to the amplitude of the signal voltage, and is slight for low volumes and comparatively great for high volumes. There is thus accomplished a simple form of automatic control.

Discussion

The nature of this control action can best be understood by a study of the oscillograms (Figs. 2, 3, 4, and 5 (Plates I and II)). Fig. 2 shows a series of eight still pictures of the amplifier output voltage when the input was a pure 300 cycle note. The pictures show conditions at approximately 1/40 sec. intervals over a period during which the input level was increased eight decibels. The first picture of Fig. 2, *a*, shows the initial output. The second shows the increased output immediately after the input level had been raised. The remainder show the action of the control in reducing the amplitude to the final level of the second last picture in Fig. 2, *c*. The last picture shows, for comparison, the increased output level that would have been obtained without any control action. The oscillograms of Fig. 3 give a continuous record of the amplifier output over a period of about one second, during which time the 300 cycle input voltage was increased ten decibels for about 3/10 sec. and then decreased again. (The ticks indicate tenths of seconds.) Fig. 3, *a*, shows the output uncontrolled. Fig. 3, *b*, *c* and *d*, show the output with the automatic control in operation. In *b* the control operates to reduce the gain on the louder signal, while in *c* and *d* (*c* and *d* are continuations of *b*),

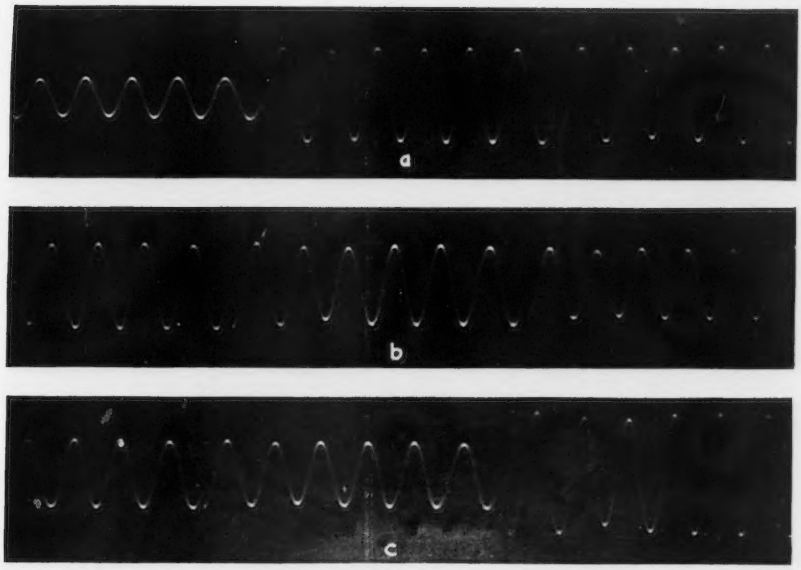


FIG. 2

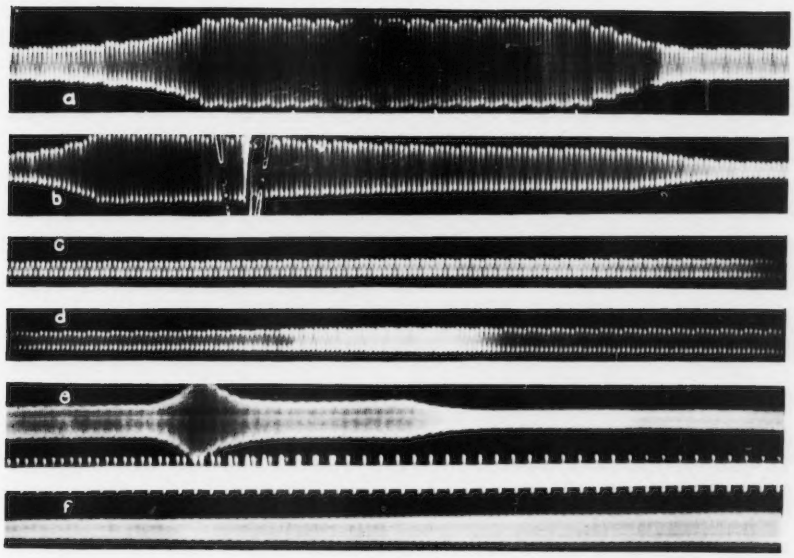


FIG. 3

FIG. 2. *A series of pictures of a 300 cycle note, the volume of which is being reduced by the control.* FIG. 3. *A 300 cycle note during a sharp increase and decrease in volume. (a) Without the control; (b, c and d) with the automatic control; (e and f) with the control and using very short time constants.*

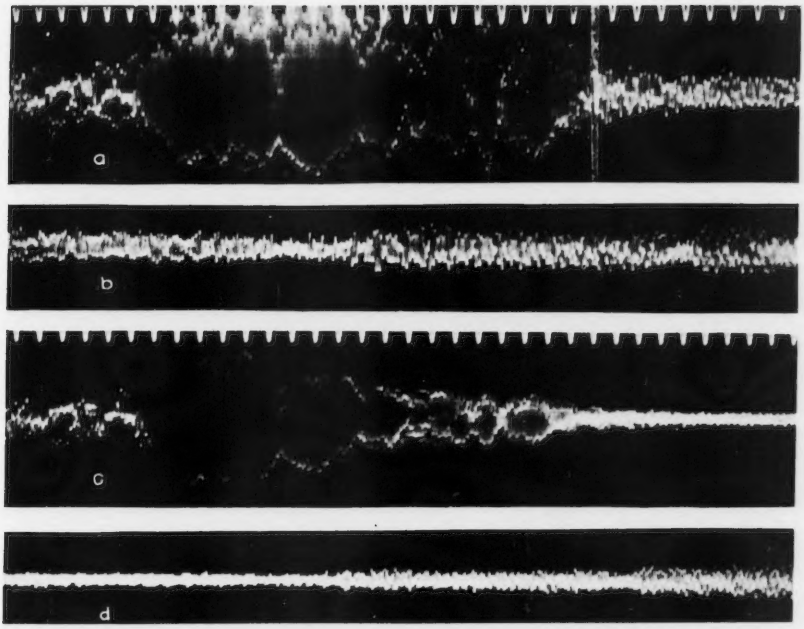


FIG. 4

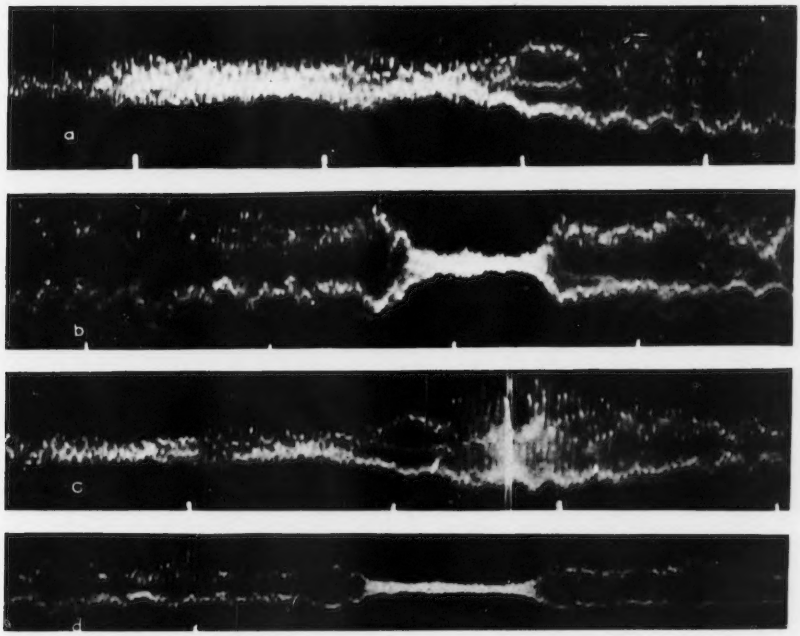


FIG. 5

FIG. 4. *A soprano voice on a sudden high peak. a and b, without the control; c and d, with the control.* FIG. 5. *A baritone voice on a crescendo passage; a and b, without the control; c and d, with the control.*

the gain is being slowly increased by the control after the input level was decreased. Note that although it takes only about 1/5 sec. to reduce the gain on a peak it requires nearly a full second to return the gain to normal after the peak has passed. This is necessary to preserve the naturalness of reproduction. In Fig. 3, *e* and *f* are similar to *b*, *c*, and *d*, except that shorter time constants were used. Figs. 4 and 5 are oscillograms of a soprano and baritone voice, respectively, during peak passages in a song; *a* and *b* in each case show the passages uncontrolled, while *c* and *d* show the same passages automatically controlled. The timing wave of Fig. 4 is 60 cycles, while the ticks of Fig. 5 indicate 1/5 sec. These oscillograms indicate the manner in

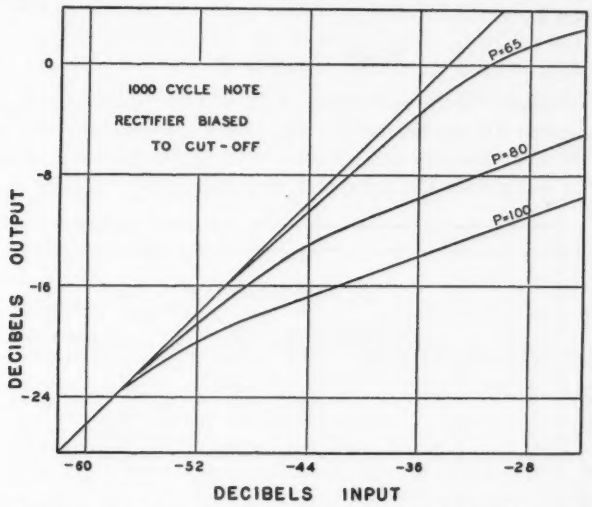


FIG. 6. *Amplifier input-output curves for different degrees of automatic control action.*

which the gain changes with variations in input level. The quantitative relation between gain and input level is given by the input-output curves of Fig. 6.

From the curves of Fig. 6 it can be seen that for all input levels up to about −60 db. the amplifier gain is constant at 34 db., but that for input levels higher than −60 db. (depending on the setting of P_1) the gain is reduced by an amount that depends on the average volume level of the signal. Over a small interval of time, however, this reduction in gain is the same for all components of the signal voltage, regardless of frequency or amplitude. The slope of the curve indicates the contraction that will occur in the output volume range. In practice if the slope is not great enough, that is, if the contraction is too large, the output will be of almost a constant level and the music will lack "depth" and "contrast"; on the other hand, too great a slope, approaching unity, will give insufficient control action. The setting of P_1 determines the strength of the control action for a given output voltage, and

so for a fixed rectifier bias determines the output voltage at which the control becomes effective. It will be seen from Fig. 6 that the slope of the upper portion of all the curves is almost the same, and, therefore, independent of P_1. For an amplifier with a variable-μ tube, the following relation holds fairly approximately over the operating range of the tube—

$$E_0 = \frac{K}{V^a} E_i ,$$

where E_0 = output signal voltage, E_i = input signal voltage, V = grid bias on the tube, K is a constant, and a is a parameter of the variable-μ tube. From this relation it can be shown that the slope of the input-output decibel curve is given by

$$\text{Slope} = \frac{1}{pa + 1}$$

where p is constant for the rectifier used ($p = 1$ for linear rectification, and $p = 2$ for square law rectification). Because a is determined by the choice of variable-μ tube, the only other means of changing the slope of the input-output curve is through the type of rectification used. Curve 2 of Fig. 7

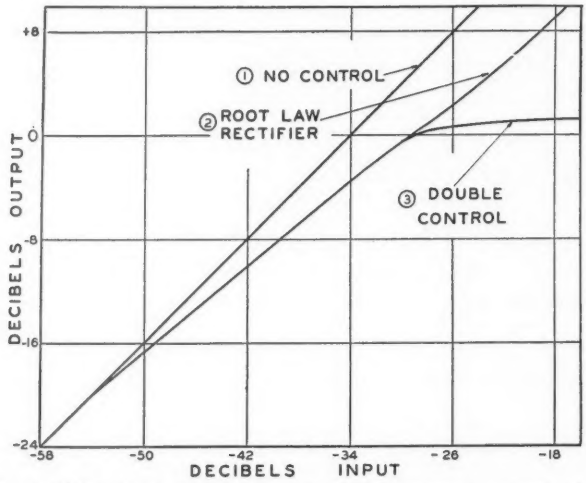


FIG. 7. *Amplifier input-output curves. 1. Without automatic control. 2. With the control of Fig. 1 using a root-law rectifier. 3. With the control of Fig. 8.*

shows an increased slope obtained by the use of a rectifier whose output varied approximately as the square root of the input voltage. This curve is very nearly straight over a 34 db. range. A control action that possesses the cut-off characteristic shown by Curve 3 is effective in limiting the amplifier output to a predetermined maximum (say, corresponding to 100% modulation) and so gives a "safety valve" action as well as the gradual control over the normal range. It may be obtained with the circuit of Fig. 8 in which a

high gain tube is connected in parallel with the usual rectifier but arranged with a larger bias, so that it does not become operative until the desired output voltage is reached. Fortunately, however, the simple circuit of Fig. 1 gives a control action quite satisfactory in practice.

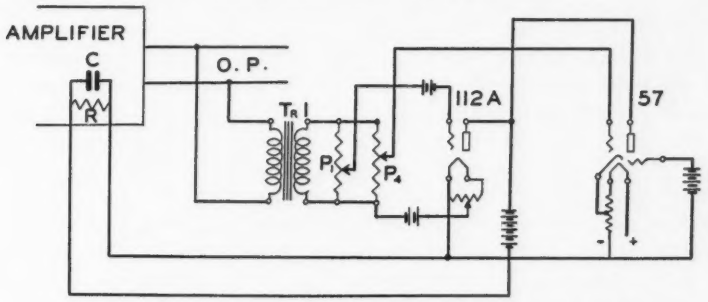


FIG. 8. *A control circuit giving an added "safety-valve" action.*

The smooth operation of the control depends largely upon the selection of suitable time constants. These are the times to (i) reduce or (ii) increase the gain when the input level changes. The first is the time required to charge the condenser C through the plate resistance of the rectifier (although the shunt resistance R decreases this slightly), while the second is the time required to discharge the condenser through R. Too long a time for (i) makes the control sluggish and slow, while a very short time gives too sharp a reduction, and produces, on high peaks, a throttling or choking effect similar to that observed when the manual control is operated too quickly. This time should be longer than one-quarter of the period of the lowest note it is desired to amplify. The time required to raise the gain on a soft passage after a louder passage has passed is important. If too short a time is used, say 1/10 sec., the control increases the volume too rapidly on a soft passage and some of the artistic effect is destroyed. If a very long time-constant, such as five seconds, is used, then, when the gain is decreased by a high peak it remains at this reduced level for so long a period that, if these peaks occur at all frequently, the average level of the program will be maintained too low. The optimum value for this latter time however is not too critical and was selected as 0.8 sec., although any time within the range of $\frac{1}{2}$ to 2 sec. is fairly satisfactory.

For such a control to be acceptable as part of a broadcast amplifier it is essential that the amplification remain distortionless. At those times when the input signal level to the amplifier is relatively steady, the control bias on T_1 is constant, and the amplifier operation, as far as phase, amplitude, and frequency distortion are concerned, is identical with the uncontrolled operation except for the increased bias on tube T_1. The primary winding of the inter-stage transformer Tr_2 is shunted by a resistor R_2 of a value approximately equal to the plate resistance of the replaced triode, so that the frequency response of this stage remains unchanged. The filter circuit C, R, C_1, R_1,

between input and output effectively prevents regeneration or degeneration effects. However, during those periods when the amplifier gain is changing from one level to another the question of transitory distortion arises. To investigate conditions during these transition periods the oscillograms were taken. Those of Fig. 2 show the wave form of a 300 cycle note immediately before and during a transition period. The only discernible difference is the gradual decrease in amplitude, the trace retaining its pure sine wave shape. The continuous film oscillograms of Figs. 3, 4, and 5 show how the wave envelope expands and contracts with the changing bias without affecting the shape of the individual waves. From Fig. 3, *a* and *b*, is obtained a comparison of manual and automatic control. Fig. 3, *a*, shows the result of a rather rapid manual operation. The increase and decrease in amplitude take place in small but discontinuous steps. With automatic control (Fig. 3, *b*, *c*, and *d*) the amplitude decreases and increases gradually according to an exponential law Ae^{-z}, and the action is seen to be much less abrupt and therefore less noticeable than that of the manual control. The automatic volume reductions shown in Figs. 4 and 5 occurred on very sudden high peaks, and are more rapid than is usually the case, but they were taken to show the control under the most severe conditions. The changes in gain occurring normally are so gradual as to be imperceptible in an oscillogram covering only one or two seconds.

The operating technique with the control functioning is simple. As before, the manual attenuator control is opened at the beginning of each selection, and, with the aid of the volume indicator, Ma_2, and control action indicator, Ma_1, is set at approximately the correct position for the particular selection. The automatic control then keeps the volume range within the desired limits. Should the operator err in his judgment and set his gain too high, there is no unpleasant blasting as would result ordinarily—he merely observes on meter Ma_1 that the control action is stronger than normal and reduces it at his leisure.

Conclusions

The curves of Fig. 6 indicate that the control action of the simple circuit of Fig. 1 is not fully automatic. The volume contractions occur only on the upper 30 db. of the complete 60 or 70 db. range. A completely automatic control, *i.e.*, one that would contract uniformly a 70 db. range to 30 or 40 db., might be obtained with a more complicated circuit, but such action is not desirable. It would necessitate reductions in volume too great to pass unnoticed, and the in-between-selection noises (artist's movements, rustle of pages, etc.) being transmitted at maximum gain would prove objectionable unless reduced manually. The presence of an operator is essential, but the semi-automatic gain control will perform for him the continual controlling throughout the selection.

Acknowledgment

The writer wishes to express his sincere thanks to Dr. H. J. MacLeod for supervising the investigation.

THE RADIAL-STEREOPLOTTER[1]

By E. L. M. Burns[2] and R. H. Field[3]

Abstract

A machine for plotting from air photographs, by the radial line method, has been developed by the Associate Research Committee on Surveys. The purpose of the plotter is to increase the accuracy and speed of extending minor control through strips of photographs by this method which is so widely used in Canada.

A description of the machine is given, preceded by a brief explanation of the principles underlying its design.

The methods so far employed in using the plotter are explained together with an examination of the sources of error arising in these methods, some of which are of general application to radial line plotting. Owing to the short time that the radial-stereoplotter has been in operation, conclusive statements cannot be made as to the results it will give when handled by an experienced operator, but already there is evidence of a considerable saving of time and gain in accuracy as compared with hand graphical methods of extending radial line control.

Introduction

The Subcommittee on Mapping Methods of the Associate Research Committee on Surveys, in its efforts to develop those forms of air photogrammetry peculiarly applicable to Canadian conditions, *i.e.*, the need for small-scale maps produced as cheaply and efficiently as possible, has sponsored the construction of a machine for extending control by radial intersection through strips of air photographs. The principles of the plotter were developed by Colonel Burns, and the design and construction of the first model was undertaken by the staff of the National Research Council in co-operation with him.

Radial Intersection Control

The radial line method of extending control is now well established. It is discussed in References (1) and (2), and depends on the fact that for the case of vertical air photographs the distortion due to elevation differences and to small tilts may be regarded as radial from the principal point (2, p. 69). This permits nets of triangles to be extended through a strip of overlapping photographs, the corners of the triangles being formed by the ground plans (plotted to a uniform scale) of the principal points of consecutive photographs and of convenient details near the margins (minor control points). The points so plotted form a system of control for the transfer of detail from the photographs to the map.

Fundamental Considerations

Let Fig. 1 represent two consecutive vertical (untilted) photographs placed so that the principal point of the right-hand photograph, P_1, is placed over the image of the corresponding detail in the left-hand photograph, and one

[1] *Manuscript received March 20, 1937.*
Contribution from the Division of Physics, National Research Laboratories, Ottawa, Canada, and the Geographical Section, General Staff, Department of National Defence, Ottawa.

[2] *Formerly General Staff Officer, Surveys, Militia Services, Department of National Defence, Ottawa, and Convener, Subcommittee on Mapping Methods, Associate Committee on Survey Research, National Research Council of Canada.*
[3] *Physicist, National Research Laboratories, Ottawa.*

of the photographs is rotated about this point until the image of the detail corresponding to P, the principal point of the left-hand photograph, falls on the line PP_1; PP_1 is the projection of the air base, or line joining the two positions of the camera lens at the respective instants of exposure. Let A represent the image of a detail on the ground as registered on the left-hand photograph, and A_1 represent the image of the same detail on the right-hand photograph. If the photographs were untilted, undistorted, taken at the same altitude and the elevations of the three points P, P_1, and A were the same, A and A_1 would coincide. If this does not occur, and the tilt is small, the point a where AP and A_1P_1 intersect is the ground plan, to the scale set by the length of PP_1, of the detail represented by A with respect to PP_1. Perspective considerations show that A_1A is parallel to PP_1, for it is the trace on the photographs of a plane passing through the lens and parallel to PP_1. Relative tilt in the photographs will cause a departure from this parallelism.

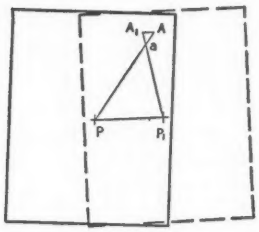


FIG. 1.

With the photographs placed as in Fig. 1, a linkage could be imagined consisting of two rods, pivoted respectively at P and P_1, which would serve to determine the true shape of triangles formed by the ground plans of the points P, P_1, and A. To make such a scheme feasible it would be necessary to separate the photographs so that both were visible at once, and conditions would become as indicated in Fig. 2. The right-hand photograph is moved

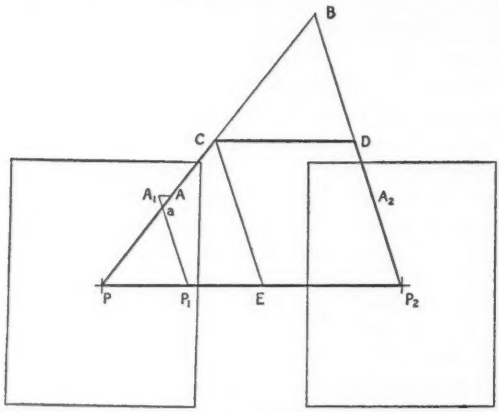


FIG. 2.

by an amount P_1P_2, and A_1 moves to A_2. Produce PA and P_2A_2 to intersect at B. The triangle BPP_2 is similar to the triangle aPP_1. This is quite general, and as the two radial arms PA and P_2A_2 were directed over the corresponding images of ground detail, the various positions of B would,

if plotted, form a figure similar to that traced by the various positions of a, with the photographs superimposed as in Fig. 1. The scale of the plot of B's positions is obviously $\frac{PP_2}{PP_1}$ times the scale of the plot of a's positions. It follows, with the method visualized, that the scale can be adjusted by altering the length PP_2, but it is impracticable to reduce the scale to the extent that the photographs touch each other.

The scale may be reduced still further by the following modification. Draw CD parallel to PP_2, intersecting the radial lines in C and D. Draw CE parallel to P_2A_2, intersecting PP_2 in E. If CD remains parallel to PP_2 and of a constant length, as B moves from point to point, the triangle CPE will always be similar to BPP_2, and therefore C will trace a similar figure to B, but at a scale $\frac{PE}{PP_1}$ of the scale of the figure traced by a. In this way, by choosing the fixed length of CD we can arrange so that any convenient point in it (to which a pencil could be attached) would plot the plan positions of the detail registered on the overlapping photographs to a scale such that the air base was represented by the length $(PP_2 - CD)$.

In the radial-stereoplotter it is not practicable to use all parts of the figure CDP_2P in one plane, but the arms PA and P_2A_2, which determine the angles APP_1 and A_1P_1P, are in one plane, and in another, the arms CP and DP_2 move respectively parallel to them. The link or bridge CD is adjustable to determine the plotting scale, *i.e.*, by making the lines joining the plotted positions of selected points coincide with the lengths already plotted from the previous pair of photographs. The scale is chosen by setting the length of CD equal to a convenient amount when the first pair of a strip is plotted.

This device may be considered as an adaptation of the well known Zeiss parallelogram, so named about the time it was first used by Pulfrich and his assistants in the Zeiss Stereo-autograph for plotting terrestrial photographs. A further discussion of its properties will be found in References (2) and (5).

Principle of the Radial-stereoplotter

Imagine two consecutive photographs (a stereoscopic pair) oriented so that the air base lies along PP_1, Fig. 3, *i.e.*, set in the same relative orientation as at the respective instants of exposure, all tilts being ignored. In the plotter, the photographs are clipped on tables and have the principal points set over the centres of rotation, so that this adjustment is easily made (2, p. 34). A magnifying stereoscope D is provided with mirrors M and M_1, and by means of a right- and left-handed screw the distance MM_1 can be altered until it is possible to set the stereoscope so that the images, A and A_1, of a given detail are focused respectively on the reticules of the left- and right-hand telescopes of the stereoscope. The reticule marks (floating mark) of the stereoscope will then appear to lie on the ground at the point in question (2, p. 26) according to the well known principles of stereoscopy.

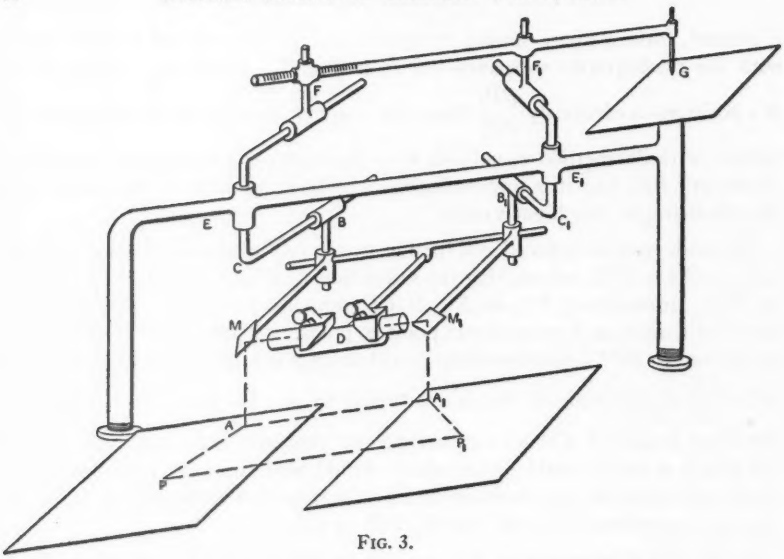


FIG. 3.

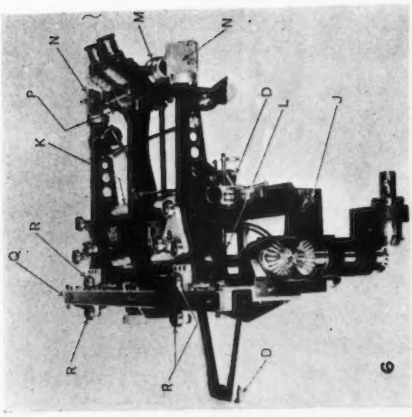
The brackets carrying the mirrors bear pivots at B and B_1, the upper parts of these pivots being fitted with slides on which engage arms CB and C_1B_1, which are free to swing about fixed pivots at E and E_1. The mirrors are adjusted until B is under E, when the left telescope is directed on P, and similarly for the right telescope. The horizontal projections of EE_1 and PP_1 then form a rectangle, and it is readily seen that the horizontal projection of EBB_1E_1 is similar and equal to that of PAA_1P_1, *i.e.*, we have the figure PAA_2P_2 in Fig. 2.

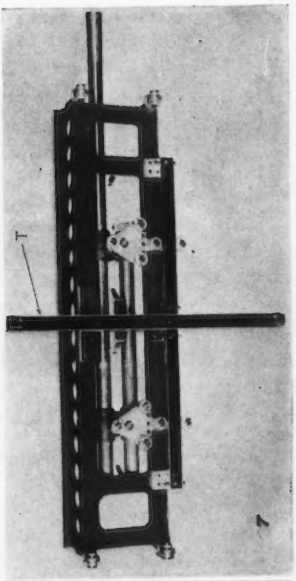
For plotting purposes two additional radial arms, above the pivots E and E_1, move parallel to the lower arms. A bridge FF_1G, constrained so as always to remain parallel to EE_1, is fitted with pivoted slides at F and F_1 in which the upper radial arms engage, thus forming a "Zeiss parallelogram". Any point on FF_1G, say G, will plot the relative plan positions of the points properly sighted on by the stereoscope to a scale at which the length, $(EE_1 - FF_1)$, represents the horizontal projected length of the air base PP_1. This scale may be quite different from that of the photographs.

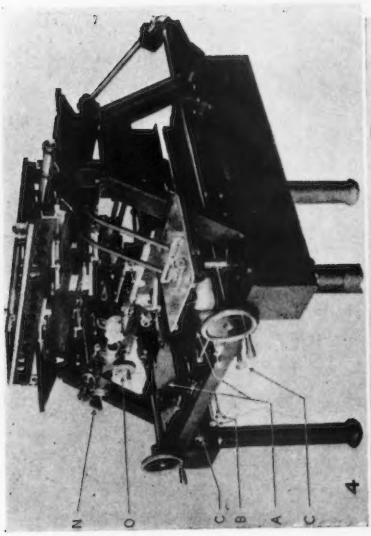
PLATE I

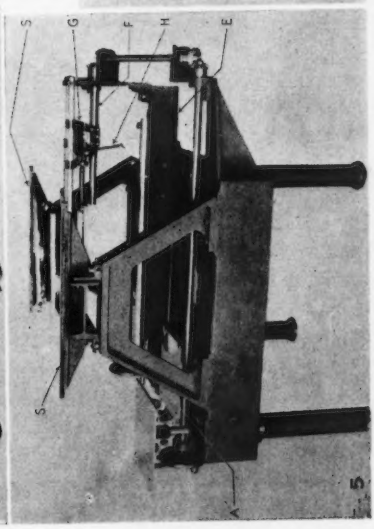
FIG. 4. *The radial-stereoplotter.* FIG. 5. *The plotter without the upper and lower carriages. The upper radial arms, their fixed pivot bearings, and the plotting table are visible, as well as the handwheel and most of the mechanism for moving the lower carriage slowly in the Y direction.* FIG. 6. *The lower carriage, showing the mechanism for moving the stereoscope along the carriage in the X direction. The stereo telescopes and the mirror brackets, with the pivots which engage with the lower radial arms, are seen, as well as the two tubes along which the mirror brackets slide when parallax (Z direction) adjustments are made.* FIG. 7. *The upper carriage. The X and Y direction guide bars are clearly seen, as well as the triangular plates on the end of the pivots which engage with the upper radial arms. The spacing of these pivots determines the plotting scale. The plotting pencil is carried from the tube seen extending to the right.*

PLATE I









It should be observed that the radial intersection method of plotting fails when the two rays tend to approach the same direction, *i.e.*, along the air base. With the radial-stereoplotter it is possible to plot accurately the positions of the principal points themselves, but between them is a sort of lune within which points cannot be plotted with precision. This figure covers the area where the angle between the radial arms is 150° or greater.

Description of the Radial-stereoplotter

General

With the aid of the foregoing somewhat abbreviated explanation of the principles of the plotter, it will be possible to follow its construction. The main problem in design was to provide a number of sliding members without introducing backlash on the one hand, or, on the other, forces of sufficient magnitude to limit the free working of the machine or to strain any part to the extent that the accuracy would be impaired. This latter consideration, while to some extent self-evident, had been emphasized in some investigations on factors affecting the precision of first-order theodolites, carried out at the National Research Laboratories a short time ago (4).

The problem was met by constructing all moving parts as light as possible, and employing ball bearings to act as rollers at many of the sliding contacts. One also attempted to reduce the arms of couples to a minimum. When the machine had been constructed it was found that these efforts, coupled with the first-class workmanship contributed by the Instrument Shop, had been successful to the extent that operation is exceedingly free and smooth, with imperceptible backlash.

The machine is illustrated in Figs. 4, 5, 6 and 7. In Fig. 4 the complete plotter is shown, Fig. 5 is a view with the upper and lower carriages removed, Fig. 6 shows the lower carriage, bearing the stereoscope (seen from one end), and Fig. 7 is an underneath view of the upper, plotting carriage.

Two tables *A* (Figs. 4 and 5), mounted on pivots with centres 18.5 in. apart, hold the photographs. These tables can be clamped, released, and rotated freely by hand, or rotated slowly by screws *B*, acting on the clamping screws *C*, following somewhat the system used in transits. Fine needle holes indicate the centres of rotation of the tables, and spring clips serve to hold the photographs in place. This portion of the machine follows lines that have been successfully applied to simple stereoscopes designed for government survey offices at Ottawa.

The right-hand print table can be moved in a direction perpendicular to the base for the purpose of measuring want of correspondence in this direction. This is accomplished by mounting the pivot housing in slides, with gib and screws for taking up slackness. Movement of the table is controlled by a screw butting against the front of the housing and a spring and plunger at the rear. A scale and vernier measure displacements, and permit the table to be reset for plotting purposes.

An I beam, on its side, is used to support the main pivot bearing housings for the radial arms (*E*, Fig. 3). These bearings are also spaced at 18.5 in. centres and each consists of two torque-tube ball bearings, $2\frac{5}{16}$ in. bore. The radial arms are located by keys cut out of the solid ends of the pivots and are ground parallel. The centres of the pivots and of the tables are adjusted so that their horizontal projection forms a rectangle. This, as well as all the other adjustments necessary to secure accurate working, can be made directly by observations carried out with the aid of the stereoscope telescopes or other parts of the plotter. Adjusting screws are provided for bringing the different slides into parallelism and otherwise correcting the various geometrical relations of the elements of the machine to secure accurate performance.

Lower Carriage

The lower carriage, Fig. 6, is supported on three rollers, consisting of commercial ball bearings fitted on eccentric pins to permit adjustment. It is guided in the *Y* direction (*i.e.* perpendicular to the air base) by four similar rollers *D*, which engage with the sides of a fixed, rectangular section bar carried on a light I beam *E* (Fig. 5), and which also forms a rail for the central supporting roller of the carriage. The body of the carriage is an aluminium casting and is moved in the *Y* direction by means of a screw *F*. A sliding piece *G*, carried on two bars parallel to *F*, is fitted with a half nut which can be engaged with *F* or released by an arm *H*, linked to a lever *J* (Fig. 6) conveniently located at the end of the carriage. The coupling between *G* and the carriage is a strut fitted with spherical ends so that direct pull or push forces only can be transmitted.

The screw *F* is coupled to a handwheel, placed conveniently at the observer's right hand, by means of the shafts and bevel gears seen in Fig. 5, and which are mounted in ball bearings, with ball thrust for the screw, to permit smooth, easy operation of the carriage to its final setting during an observation.

The stereoscope may be considered as composed of three parts, mounted on two thin-walled steel tubes *K* and *L* (Fig. 6). The central portion, fixed to the middle of the tubes, bears the two telescopes. Optically, each telescope consists of an objective (25 mm. diam.), two prisms to erect the image and present it to the eye at a comfortable inclination (20° above horizontal), a glass diaphragm ruled with one-half the floating mark and an eyepiece giving a magnification of about 2.5×. The objective is mounted in a sleeve, focused by means of a nut, *M*, engaging with two portions of a screw fitted in slots on the telescope tube 180° apart. The eyepieces can also be focused and their spacing varied to suit individual observers. This latter adjustment is made by a right- and left-handed screw, and, when it is completed, clamping screws enable the telescopes to be clamped firmly on the slide carrying them.

Stainless steel mirrors, *N*, 50 by 50 mm., each spring-constrained against the points of three adjusting screws, are held on the two outer brackets of the stereoscope, which also bear the pivots corresponding to *B* and B_1 (Fig. 3). These pivots consist of spindles each carried in two self-aligning ball bearings,

and fitted at its upper end with a triangular plate of duralumin on which are mounted three horizontal rollers (non self-aligning ball bearings). Eccentric pins are used to carry these rollers so that the axis of rotation of the pivot can be made to coincide with the axis of rotation of the lower radial arm with which the rollers engage. By adjustment the telescope diaphragms are brought to focus on points at the same spacing as the axes of the pivots, thus conforming to the relations illustrated in Fig. 3. Adjustment of this spacing (parallax change) is effected by means of a right- and left-handed screw, parallel to and placed between the tubes *K* and *L*. A quadruple-threaded wormwheel at the centre of this screw, mounted in the central bracket of the stereoscope assembly, engages with a worm on the same shaft as the handle *O* (Fig. 4). The right-left screw is cut with a vee thread, and the nuts on the outer brackets are split, so that these brackets, which are fitted with lapped bushings for the tubes *K* and *L*, slide along the tubes without backlash or the necessity of any clamping device, which, indeed, would introduce difficulty owing to the frequency with which changes in parallax settings have to be made.

Slow movement of the stereoscope as a whole in the *X* direction on the carriage is controlled by a screw with a disengaging half-nut on the central bracket, linked to the small lever *P* (Fig. 6). The gearing and quill seen at the end of the carriage in Fig. 6 permit the screw to be operated from a shaft with handle set at the observer's left hand. The quill transmits a torque only, so that non-alignment of the shaft does not introduce friction.

Motion of the stereoscope in the *X* direction is governed by a slide, *Q*, made for convenience in grinding, from two pieces, and carried on brackets mounted on the rear of the carriage. Extensions on the mirror brackets carry rollers *R* which engage with the two opposite ground faces of this slide, which is placed as closely as possible to the plane of the lower radial arms. The weight of the stereoscope is supported by two rollers beneath each of the mirror brackets, and it was found necessary to mount a small roller under each bracket, at the rear, to resist a lifting tendency when the machine was operated.

Graduated scales are provided for indicating the change in spacing between the mirror brackets (parallax)—which can be read to 0.02 mm. by means of a vernier—the displacement of each mirror bracket in the *X* direction, and the displacement of the carriage in the *Y* direction; these latter scales can be read to within 0.1 mm. Lenses mounted in front of the verniers permit the scales to be read comfortably from the observer's seat.

A constant illumination of the portion of the picture covered by the field of view of the stereoscope (65 mm. diameter) is obtained by mounting an automobile headlight bulb on each mirror bracket.

Upper Carriage

The upper, or plotting carriage, is simpler than the lower one. It is likewise a light aluminium casting and is supported on four rollers running on two rails, *S* (Fig. 5), carried on brackets bolted to the I beam flanges. Two

additional brackets, at the centre of the beam, are mounted with horizontal rollers in which engages the parallel bar T (Fig. 7), rigidly attached to the bottom of the carriage, and serving to guide the motion in the Y direction. The upper radial arms engage with rollers carried on pivots similar to those used in the lower carriage, and housed in light castings fitted to two thin-walled steel tubes. The right casting is fixed to the tubes, while the left one can slide to alter the spacing, *i.e.*, set the plotting scale of the Zeiss parallelogram. This setting is made by a screw above the tubes, the right end of which fits in a journal bearing on the casting, while the left end threads in a split nut, which can be clamped when the setting is made. A scale and vernier indicate the inset, or base length, in millimetres (*i.e.*, the length PE in Fig. 2). Each casting is supported on two rollers, running on ground steel rails, as in the case of the lower carriage, and the X direction guides, seen in Fig. 7, are also similar.

One of the steel tubes extends through the end of the carriage, and to it is attached a light truss bearing the plotting point. The plotting pencil, at the lower end of this truss, was made to fit on a slide with a rack and pinion to adjust the pencil by aid of a scale and vernier. This arrangement was to permit plotting with the centre of either photograph table as origin, but in practice it has been found best always to use the right photograph.

A table, fitted in a pivoted support with a clamping screw, serves to hold the paper. This is used in the form of a roll, the unused portions being held in light brackets beneath the table. Spring clips hold the paper in position during plotting. The plotting table is placed conveniently to the observer's right, and is visible in Figs. 4 and 5.

Experience would indicate the desirability of fitting a sighting microscope, for use in place of the pencil, when adjusting the plot to the photographs.

Method of Plotting Control with the Radial-Stereoplotter

(a) Photographs are set by centering the floating marks in turn on the engraved crosses that mark the centres of rotation of the photo-carrying tables, and then placing the photograph principal points under the floating marks.

(b) The photographs are oriented along the line joining their principal points, which will hereafter be called the base line. This is done by observing points of detail near each principal point in turn, and rotating the other photograph until vertical parallax disappears. The instrument gives a sensitive determination of vertical parallax (or want of correspondence), owing to the form of its floating mark. The forms of the marks are as shown in Fig. 8, a. Observed stereoscopically, the vertical lines fuse, and, when there

FIG. 8.

is no vertical parallax present in the plastic model (stereogram) against which the mark is viewed, the whole looks like a solid cross (Fig. 8, b). When there is any vertical parallax in the plastic model, the cross breaks up, and the horizontal lines appear separated in the Y direction (Fig. 8, c).

(c) The scale of the plot depends upon the ratio of the base-length (set on the upper carriage) to the natural distance between the objects on the ground on whose images the principal points of the photographs fall. If two points, whose distance apart is known, appear in the first overlap, the machine may be set to plot at any desired scale by first plotting the two points from the photograph with an arbitrary base-length setting. The arbitrary setting, B_1, is then corrected by multiplying it by the factor Dt/Dp, where Dt is the true distance at the desired scale, and Dp is the distance plotted at the first setting.*

(d) The machine works most conveniently when the plot proceeds from right to left of a series of photographs. When the scale has been set by adjusting the base-length as in *(c)*, two minor controls or scale control points are plotted. These should lie on a line at right angles to the base line, at a distance equal to the base above and below the left principal point. If there happens to be want of correspondence, owing to tilt, at these points, the arms of the cross constituting the floating mark will not appear collinear. When plotting the two scale control points, care must be taken to have the right arm of the cross in line with the right photograph image of the point of detail chosen, since we are performing a radial line intersection, and the angle between the line from the object to the principal point and the base line on the *right* photographs determines the Y co-ordinate of the plotted position.†

(e) The left principal point and the base line are plotted, and the base line on the plot is prolonged in both directions to the limit of the machine's movement.

(f) Points that are required as additional control for the subsequent tracing of detail are now plotted.

(g) When work with the first overlap is completed, the second photograph is transferred to the right photograph carrier, and the third photograph placed on the left one. The pair is then oriented as in *(b)* and the base lines ruled in.

(h) The plot is shifted so that the plotted principal point of the second photograph now lies on the centre of rotation of the plotting table, where the pencil rests when the floating mark is centered over the centre of rotation of the right photograph carrier. This is the origin for plotting in each overlap.

* *The base line is marked on each photograph by laying a straight-edge on stops which bring it exactly over the centres of rotation, and scoring lines with a needle point. This operation must be very carefully performed, since the azimuth of the strip depends on its accuracy, as will appear later. Accuracy may be easily checked by removing the straight-edge and moving the stereoscope along the base line, when the floating mark will show any deviation of the scored lines. The base lines are extended in both directions to the margins of the photographs.*

† *The point is identified by centering a piece of celluloid with a fine cross over it. The marker is fastened down by transparent adhesive tape. As the points are viewed stereoscopically in plotting successive overlaps, it is necessary only to identify them in this way. The actual plotting should be of the untouched point of photographic detail, as any attempt to mark it by pricking, pen, or pencil leads to loss of accuracy.*

(i) The plot must now be oriented. Regarding the successive base lines as the legs of a traverse, the angles between them will be shown on the photographs by the scored lines. We are now concerned with the angle between base 1–2 and base 2–3; this is shown on Photograph 2, and may be plotted. The plotting table is rotated through the appropriate angle, so that when the floating mark is placed on the prolongation of base line 1–2 on the plot the plotted base falls under the pencil point.

(j) It is now necessary to adjust the base-length so that the plot of the second overlap will be at the same scale as that of the first. This is done by setting the floating mark on one of the scale control points. If there is want of correspondence, the left arm of the floating mark must be in line with the left photograph image of the control point; for the same reason, *mutatis mutandis*, as given in *(d)* above. If the pencil now falls on the point as plotted from the previous overlap, the scale is correct. If there is a discrepancy, the base-length is altered until the pencil falls on the point.

(k) The scale is checked by plotting the other scale control point. If it plots in the same position as determined from the previous overlap, this proves the scale to be correct. Sometimes, however, there is a discrepancy, which may be due to some of the operations previously described not having been done with sufficient accuracy. These are checked, and if the discrepancy persists, it is due to the effect of tilt, combined with height differences, or distortion of the photograph materials. It may be observed that the instrument indicates clearly when relative tilt is present, by the want of correspondence (vertical parallax) shown by the floating mark; the magnitude and direction of tilt may also be deduced approximately.

Errors

The sources of error in plotting with the instrument, and by the radial line method generally will now be discussed, and methods will be suggested for eliminating them, or correcting the plot.

Sources of Error in Radial Line Plotting

In making a radial line plot of a series of aerial photographs, we are in effect making a graphical triangulation, using the angles between objects as shown on the photographs. The errors of the plot may be either in azimuth, or in scale, or in both. There may be an error in one azimuth angle, or a series of small errors having a cumulative bending effect on the chain of triangles; and there may be a change of scale in one overlap or a gradual change of scale, the cumulative effect of small inaccuracies. Sudden changes in azimuth or scale can be due only to mistakes, and can be detected by a simple check. The cumulative effects of small inaccuracies become apparent when the plotted strip is laid down in a compilation with the plots of adjoining photograph strips. If there are two ground control points in each end overlap of the strip, as is usually the case when control is by traverse, it is easy to determine whether a constant scale has been preserved throughout the length of the strip.

Azimuth Errors

Small errors in azimuth may be caused by:—

(a) Inaccurate centering of photographs on the carriers. The base line on the photographs will not be parallel to the base line as plotted.

(b) Inaccurate centering of principal point on plot on the centre of rotation (origin of plotting) of the table.

(c) Inaccurate orientation.

(d) Inaccurate ruling of principal point bases.

(e) Inaccurate setting off of change of azimuth on plot.

Errors due to perspective distortions in tilted photographs will be discussed later; their effects in flattish country, when tilts are less than 3°, are negligible.

The above sources of error can be largely eliminated by care on the part of the operator. The magnification of the photograph image, and the apparent magnitude of the floating mark, are such that it is possible to set the photograph in place to an accuracy of 0.03 mm.; base line orientation should be accurate to less than two minutes of arc. The thickness of the base lines scratched by needle point is about 0.10 mm., and any departure from straightness may be detected by moving the floating mark in the X direction over the *p.p.* base.

Errors *(b)* and *(e)* depend on the accuracy with which the pencil point can be placed over a previously drawn line. The thickness of the pencil lines is about 0.10 mm. With the aid of a magnifying glass, the pencil may be set to about this degree of accuracy. It is likely that the setting could be improved if a magnifying optical sight were available to replace the pencil for the adjustment, as in some continental plotting machines.

Experience shows that plotting by the machine holds azimuth accurately, as a rule, in flattish country. Long straight roads or railways, extending through several photographs, preserve their alignment. More difficulty has been found in keeping the scale constant throughout a strip; in many that were plotted in the early stages, variations of 0.025 between the beginning and end of a strip were found. Such errors are shown up by scaling on ground control at the ends of the strips, and by the fact that there are discrepancies between the positions of tie points plotted from adjoining strips. The same sort of errors have been met with in radial line plotting by ordinary graphical methods, and it was in the hope of eliminating these, and lessening the amount of adjustment necessary during compilation, that the radial-stereoplotter was devised.

Scale Errors

The scale is preserved, from overlap to overlap, by plotting the position of two lateral scale control points (minor control points) in one overlap, and then adjusting the base length of the succeeding overlap so that these points are plotted in identical positions. The accuracy with which this process can be carried out depends on the following factors:—

(a) Accurate identification, from overlap to overlap, of the points of detail serving as scale control points.

(b) Definition and magnitude of the points of detail.

(c) Accuracy of pointing from the principal point to control point: *i.e.*, accuracy of measurement of the angles used for intersection and resection.

(d) Accuracy of orientation, and fineness of the setting of the plotting pencil.

The effects of tilt on the preservation of scale will be discussed later.

An important advantage of the radial-stereoplotter is that the direction lines are fixed when the operator observes the images of the control points in both photographs stereoscopically. This eliminates the errors in identification, which occur when points in successive photographs are established by inspection. The next factor in securing accuracy of pointing is the definition of the point of detail. Artificial detail, such as the intersections of roads, corners of buildings, etc., is best; but much Canadian mapping is of areas where there is no artificial detail, and natural objects such as trees, rocks and so on, seldom show as sharply as one would wish. The operator must take care to choose an object on which he can point to within 0.10 mm. or less, if at all possible.

It is best not to actually mark the object by pricking or in any other manner, as this spoils the stereoscopic impression, as explained above. If the foregoing precautions are observed, it is possible to make pointings to an accuracy of 0.1 mm. or less.

If the floating mark is not brought to exactly the same parallax as the photograph image, the discrepancy in X is reproduced in the Y direction. It is, therefore, necessary to be careful in making coincidence; if want of correspondence is present, it should be eliminated by the differential Y motion of the right photograph carrier; after the floating mark is adjusted to the correct parallax, the difference in Y is restored, as pointings would otherwise be incorrect to any objects not on the ordinate through the right principal point.

With the usual conditions applying to Canadian air surveys—scale control points about 70 mm. from the principal point and a camera focal length of 210 mm.—an error of 0.1 mm. in plotting the scale control points will introduce a scale error of 1/700 or 0.0014. Unless the operator has some idiosyncrasy in pointing, the errors will be random, and tend to cancel out. A strip that showed a total scale change of more than 0.005 from one end to the other would, if reduced according to its over-all scale, put control points towards the centre out of position by about a millimetre—53 ft. at the usual scale of plotting, which is 1/15,840. While errors of this magnitude would not matter in mapping certain types of country, it is desirable to be able to eliminate them when greater accuracy is desired. In such a case, the strip would have to be plotted again; or a special adjustment made to correct for the effect of the scale variation.

The Effect of Tilt in Flat Country

If we take the case of three photographs of flat country, numbered 1, 2 and 3, of which 1 and 3 are untilted, and 2 is tilted to the right in the direction of the base line, the condition would be as shown in Fig. 9. V_2 is

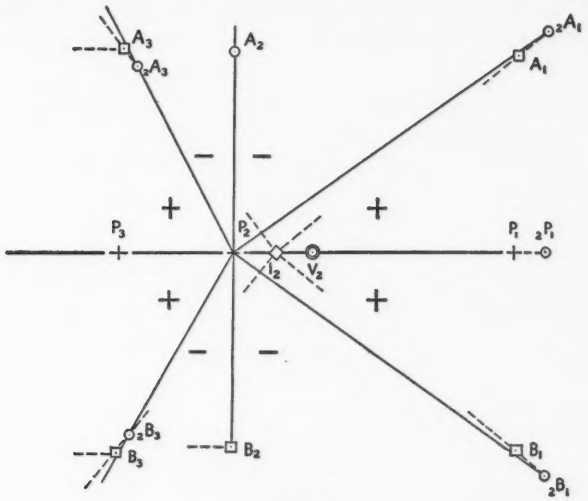


FIG. 9.

the plumb point of the second photograph, and I_2 its isocentre. Angles about its principal point will not be true. If the isocentre, I_2, could be found and used as the centre of plotting, angles would be true, but it is not practicable to do this.

It will be seen that the angles ${}_2A_1P_2P_1$ and ${}_2B_1P_2P_1$, and also ${}_2A_3P_2P_3$ and ${}_2B_3P_2P_3$ are larger than they should be. The ratio of the tangents of these angles to the tangents of true plan angles is sec θ, where θ is the tilt (3, Art. 17). The complementary angles will be too small, and in Fig. 9 a plus or minus sign has been placed to indicate the tilt effect on the angles in each of the eight sectors into which the photograph is divided by lines drawn to the surrounding control points.

It is clear that if the strip is oriented along the base lines there will be no error in strip azimuth; but a difference of scale will be introduced.

As the angles between A_1, and P_1 and B_1 are too large on photograph 2, when the position of P_2 is determined by resection it will be too close to P_1. The ratio of the plotted base line P_2P_1 to its true length will be cos θ. When A_2 and B_2 are intersected, the scale along A_2B_2 will be too small (in the same ratio) as it depends on the base P_2P_1; when P_3 is resected, the base P_3P_2 will be short, since it has been established from the line A_2B_2, which is short. But A_3 and B_3, which are intersected by the angles $A_3P_2P_3$ and $B_3P_2P_3$, which are too great, will be in their correct position and the scale will be re-established.

Tilts in gyropilot-controlled aircraft are seldom as great as 3°, and if the cosine of 3° is applied to 70 mm., the average base length is shortened by only 0.10 mm., a negligible amount, practically speaking.

If a line with an occasional larger tilt had to be plotted, the magnitude and direction of the tilt could be estimated (2, pp. 140–147), and after resection from the photograph, the base length could be increased by the amount required.

Inspection of Fig. 9 will show that if the direction of tilt were transverse to the line of flight, the angles with which resection and subsequent intersection are made would be too small, and the base lengths and scale generally in the two overlaps in which the tilted photograph figured would be too large, coming back to normal with the next untilted pair.

If the direction of tilt is at 45° to the base line, one of the resection angles will be too great, and the other will be too small. The position of P_2 will not be properly resected unless allowance is made for this, and the pointing to the photograph detail is slightly varied accordingly. There will be no error in azimuth introduced. This case of tilt is the most troublesome in practice.

Tilt and Elevation Differences

Fig. 10 is a diagram of the plan position of the principal points of three photographs, the centre one of which is tilted laterally. V_2 is its plumb point. If the point of detail upon which P_1 falls is higher than the plotting

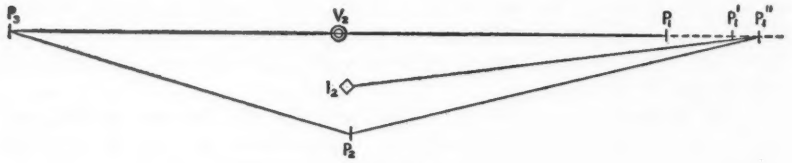


FIG. 10.

datum plane, its position will be distorted outwards to P_1'. Tilt will cause the principal point to move to P_2, and P_1' will move to P_1'' on a line radial from the isocentre. The line P_2P_1'' will therefore not give the true direction to the plan position of P_1 relative to other objects imaged in the photograph, and this discrepancy, the magnitude of which may be easily calculated, will seriously disorient the strip.

In such a case the trouble will soon show itself. The tilt will be indicated by want of correspondence; and its direction and magnitude, and hence the approximate plumb point, can be estimated by methods described by Major Hotine (2).

The overlaps where the difficulty occurs could then be plotted again, by use of the approximate plumb points so found, instead of the principal points.

Results Obtained with the Instrument

At the date of writing, the radial-stereoplotter has been in use for only about two months. Most photogrammetric machines can, in a special test, be made to give an output and accuracy beyond what would normally be obtained in routine mapping with them. On the other hand, when a new instrument is brought into use, operators gradually acquire skill with it and increase their output. It is, therefore, not possible to state finally to what degree the radial-stereoplotter will increase the accuracy and speed of radial line plotting. However, experience to date indicates that when plotting at 1/15,840 (4 in. to 1 mile) azimuth can be held correct in strips of photographs where the tilt is small so that the centre of a strip 750 mm. between ground control points will not be bent laterally by more than 1 mm. The scale can be held correct to about 1% from one end of the strip to the other.

In plotting a strip by machine, about 18 to 19 min. per photograph is required, including the plotting of roads and other subsidiary control for tracing. The experience in the Geographical Section, General Staff, has been that by the graphical method about 25 min. per photograph was required, time taken for plotting roads, etc., not included.

When strips are plotted to the accuracy mentioned above, an appreciable amount of time is saved in reduction, adjustment, and compilation, which, with the ordinary graphical method of plotting, takes about 16 min. per photograph.

Acknowledgments

The authors wish to acknowledge assistance and advice rendered by members of the Subcommittee on Mapping Methods of the Associate Research Committee on Survey, and particularly from Mr. R. B. McKay. Mr. W. C. May, of the instrument and model shops of the National Research Council cannot be too highly commended for the interest he exhibited when constructing the instrument, and for the valuable proposals he made for the modification of details, which contributed in a marked degree to the successful way in which the completed machine operated.

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THE DECOMPOSITION OF NITROUS OXIDE ON A SILVER CATALYST[1]

BY E. W. R. STEACIE[2] AND H. O. FOLKINS[3]

Abstract

The kinetics of the thermal decomposition of nitrous oxide on a silver catalyst has been investigated. The rate of the reaction can be expressed by the equation

$$-\frac{d}{dt}(N_2O) = \frac{K(N_2O)}{1 + b(O_2)} .$$

It may therefore be concluded that the nitrous oxide is slightly adsorbed by the catalyst, while oxygen is fairly strongly adsorbed and retards the reaction. Added oxygen affects the reaction in the manner predicted by the rate equation, in contrast to its behavior on a platinum catalyst as previously found by Steacie and McCubbin.

Introduction

The retardation of a reaction by its products constitutes an important phase of heterogeneous catalysis. The explanation of this retardation lies unquestionably in preferential adsorption of the products of reaction, which thus reduce the space available for the adsorption of the reactant.

Comparatively few heterogeneous gas reactions, however, have been thoroughly investigated from this point of view. Of these, the most thoroughly investigated is the decomposition of nitrous oxide on the surface of platinum. The reaction is

$$N_2O = N_2 + \tfrac{1}{2}O_2 ,$$

and it is retarded by the oxygen formed. Hinshelwood and Prichard (3) first investigated the reaction, using electrically heated filament catalysts at temperatures between 600° and 1200° C. They found that added oxygen had the same retarding effect as oxygen formed during the reaction, and that the rate could be expressed by

$$-\frac{d}{dt}(N_2O) = \frac{K(N_2O)}{1 + b(O_2)} . \qquad (1)$$

Schwab and Eberle (6) investigated the reaction in a similar way, but came to the conclusion that added oxygen had no retarding effect.

Low pressure measurements were also made by Cassel and Glückauf (2) and by van Praagh and Topley (5).

[1] *Manuscript received March 17, 1937.*
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In view of the disagreement regarding the mode of action of added oxygen, a thorough investigation of the reaction on a platinum sponge catalyst was made by Steacie and McCubbin (13, 14). The main facts established by their investigation were:

(1) Oxygen formed in the reaction retards it, the rate being given by Equation (1).

(2) Oxygen added to the reaction mixture diminishes K, and thus retards the reaction. (O_2) in the denominator, however, refers only to oxygen formed in the reaction, and not to oxygen added initially.

(3) Adsorption measurements show no appreciable difference between the adsorption of oxygen formed in the reaction and that of oxygen added initially. It may therefore be concluded that at least the major portion of the oxygen formed in the reaction is not irreversibly adsorbed.

(4) The reversibility of the adsorption process is further confirmed by the fact that the amount of oxygen adsorbed is not altered by evacuation at a red heat, or by preliminary burning off with hydrogen. It is also confirmed by the fact that in reaction rate experiments the time of evacuation has no effect on the rate of the following run.

Two of the above facts stand out as quite irreconcilable, *viz.*, (i) oxygen can retard the reaction in two different ways, (ii) the adsorption process is rapidly reversible. "Now it should be noticed that the rate equation given above, in the case where (O_2) refers only to oxygen formed in the reaction, is really of the form

$$-\frac{d}{dt}(N_2O) = \frac{K(N_2O)}{1 + f(\text{amount of } N_2O \text{ decomposed})} .$$

It is therefore possible that the retardation of the reaction by oxygen formed in it is partly real (inasmuch as added oxygen retards it also), but is mainly fictitious and due merely to the fact that f(amount of N_2O decomposed) is identical with f(amount of O_2 formed). Hence the retardation of the reaction by any other substance produced in it would be indistinguishable from retardation by oxygen." Steacie and McCubbin therefore concluded that the retardation of the reaction was probably due to a trace of some substance formed in a side reaction.

In view of the peculiar results obtained with platinum it appears to be worth while to investigate the oxygen retardation on other catalysts. The decomposition has been investigated on gold (4), but it is not retarded by oxygen. It has also been thoroughly investigated on oxide catalysts by Schwab and his co-workers (7, 8, 9, 10, 11), but the results are hardly comparable with those obtained on metal surfaces. The reaction has also been investigated on a silver catalyst by Benton and Thacker (1). This work, however, was only incidental in the course of another investigation, and no

conclusions as to oxygen retardation can be drawn from their results. It therefore seemed worth while to investigate the reaction on a silver catalyst more thoroughly from the point of view of the effect of oxygen on the rate.

Experimental

Reaction velocities were followed by observing the rate of change of pressure in a system at constant volume. The reaction vessel was made of Pyrex glass and had a capacity of about 175 cc. The pressure was measured with a capillary mercury manometer. The apparatus was similar to the general type that has been used in this laboratory in a number of previous investigations (12). The required temperatures were obtained by means of an electric furnace, and the temperature was measured with a chromel-alumel thermocouple in conjunction with a potentiometer. The temperature was controlled by manual regulation and could be maintained constant to within 2°.

Prior to making a run the system was evacuated to about 10^{-4} mm. by means of a mercury vapor pump backed by an oil pump. The time of evacuation was found to have no apparent effect upon the rate of the following run.

The silver catalyst was prepared by the method of Benton and Thacker. Finely divided precipitated silver oxide was slowly reduced by hydrogen over a period of 12 hr. at a temperature ranging from 25° C. at the start to 100° C. at the end. The silver oxide was prepared by precipitation from a solution of silver nitrate by the addition of barium hydroxide,the precipitation being carried out in the absence of carbon dioxide. Approximately 30 gm. of catalyst was used. Care was taken to keep the catalyst out of contact with air between experiments.

Nitrous oxide was obtained in cylinders from the Ohio Chemical and Manufacturing Co. It was fractionally distilled and stored in a large reservoir. Oxygen was obtained from commercial cylinders, and was used without purification except for drying.

Experimental Results

The catalyst was sufficiently active to produce appreciable decomposition at 375° C. It was, however, not found possible to produce as active a catalyst as that of Benton and Thacker, who were able to detect decomposition at the surprisingly low temperature of 60° C. Since the main object of this work was to investigate the effect of oxygen on the rate of the reaction, all runs were made at one temperature, *viz.*, 450° C. This temperature was chosen because the reaction proceeded at the most conveniently measurable rate. The rate of the homogeneous decomposition at 450° C. is negligibly slow, so that no complications are introduced on this account.

The catalyst showed signs of aging during the first four or five runs. After this its activity was reasonably constant.

I. The Decomposition of Pure Nitrous Oxide

The data for two typical runs are given in Tables I and II. In the tables, P represents the total pressure at any time, while x is the amount of nitrous oxide which has reacted. In calculating x it is necessary to know the total increase in pressure corresponding to complete reaction. The results of this, and of other investigations, indicate that the full 50% pressure increase corresponding to the equation $N_2O = N_2 + \frac{1}{2}O_2$ is not quite attained in practice. Allowing for this, and for the correction due to the dead space, we have assumed, throughout, that completion corresponds to a pressure increase of 45%. A slight change in this value would have no appreciable effect on the conclusions to be drawn. It will be seen from the tables that the rate of the reaction is very high at the start and that it falls off rapidly, thus suggesting retardation by the products of the reaction. For a reaction in which the reactant is slightly adsorbed and the products are moderately strongly adsorbed, we get an equation of the form which has already been shown to hold for the nitrous oxide decomposition on platinum, *viz.*,

TABLE I

DATA FOR A TYPICAL RUN

Time, min.	P, cm.	x, cm.	K_m	V
0	9.38	—	—	—
1	10.25	1.91	0.0989	1.91
2	10.88	3.30	0.0942	1.65
3	11.22	4.05	0.0818	1.35
4	11.52	4.71	0.0757	1.18
5	11.78	5.28	0.0718	1.05
6	12.00	5.76	0.0689	0.96
8	12.36	6.56	0.0670	0.82
10	12.62	7.13	0.0620	0.71
15	12.96	7.88	0.0531	0.52
20	13.24	8.49	0.0461	0.42

TABLE II

DATA FOR A TYPICAL RUN

Time, min.	P, cm.	x, cm.	K_m	V
0	29.00	—	—	—
1	30.46	3.21	0.0510	3.21
2	31.73	6.00	0.0503	3.00
3	32.60	7.92	0.0461	2.64
4	33.45	9.79	0.0447	2.45
5	34.12	11.26	0.0426	2.25
7	35.12	13.46	0.0387	1.92
9	35.88	15.14	0.0356	1.68
11	36.54	16.59	0.0335	1.51
14	37.24	18.13	0.0304	1.29
20	38.50	20.90	0.0277	1.04
25	39.24	22.53	0.0261	0.90

$$-\frac{d}{dt}(N_2O) = \frac{K(N_2O)}{1 + b(O_2)} = \frac{K(a - x)}{1 + bx},$$

where a is the initial concentration of the reactant. On integration this gives

$$K = \frac{1 + ab}{t} \ln \frac{a}{a - x} - \frac{bx}{t}.$$

If (3)

$$\frac{1}{t} \ln \frac{a}{a - x} = K_m, \qquad \text{and} \qquad \frac{x}{t} = V,$$

this becomes

$$V = (a + 1/b)K_m - K/b. \qquad (2)$$

Hence, a test of the applicability of the equation may be made by plotting K_m against V, and seeing whether a straight line is obtained. This has been done for several runs, and the curves are shown in Fig. 1. The linearity is

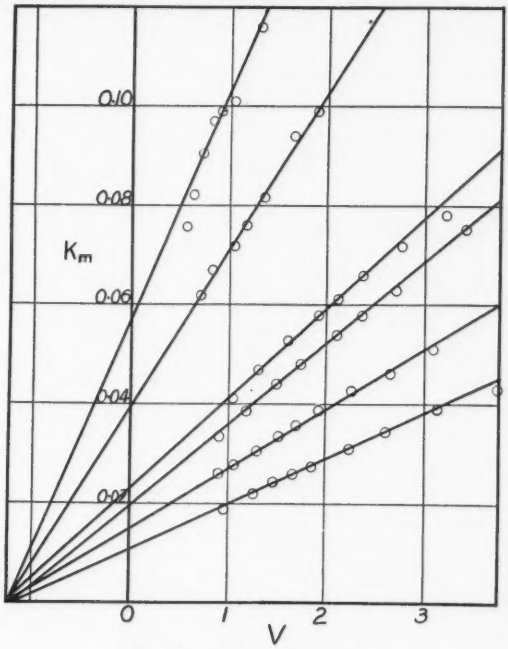

FIG. 1. *Pure nitrous oxide.*

excellent, and there is no doubt that Equation (2) fits the results. It may therefore be concluded that the reaction is retarded by oxygen on a silver surface in the same manner as on a platinum surface.

From Equation (2) we obtain for the time to one-half value

$$t_{50} = \frac{0.69}{K} + \frac{0.19\,ab}{K}.$$

Hence, if the equation fits the data over the concentration range we should obtain a straight line on plotting t_{50} against a, from the slope and intercept of which we can evaluate both b and K for the given temperature and catalyst. Table III gives the values of t_{50} for various initial pressures of nitrous oxide.

TABLE III

EFFECT OF PRESSURE ON THE RATE OF REACTION

t_{50}, min.	P, cm.	t_{50}, min.	P, cm.	t_{50}, min.	P, cm.
7.5	10.50	4.2	9.85	6.5	21.40
3.0	5.55	7.4	29.12	4.0	9.38
11.5	39.70	3.8	9.50	5.2	19.60
11.0	32.60	8.1	29.00	6.0	18.70
7.8	19.90	4.7	9.30	4.5	10.08
10.1	28.60				

The data are listed in the order in which the runs were made. Some drift is apparent in the earlier runs.

In Fig. 2, t_{50} is plotted against the initial pressure. From the intercept and slope of the line we get

$$K = 0.383 , \qquad b = 0.500 .$$

Hence the rate of reaction may be expressed by

$$-\frac{d}{dt}(N_2O) = \frac{0.383(N_2O)}{1 + 1.10(O_2)} . \tag{3}$$

It remains to be seen whether this will also fit the results in experiments in which oxygen has been added initially.

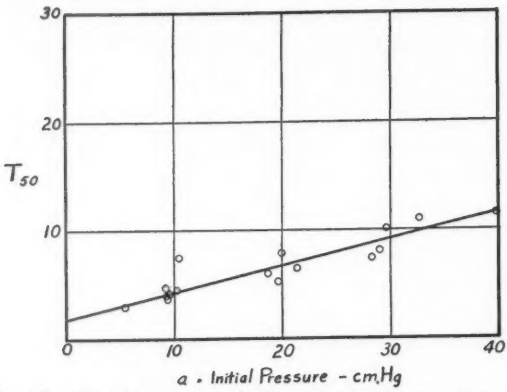

FIG. 2. *The effect of pressure on the decomposition of pure nitrous oxide.*

II. The Effect of Added Oxygen

It is apparent that if added oxygen affects the rate in the manner indicated by Equation (3), then high oxygen concentrations should be able to swamp out the effect of the oxygen formed in the reaction. The denominator will then become constant for a given run, and the rate will be given by

$$-\frac{d}{dt}(N_2O) = K_1(N_2O) .$$

In other words the retarding effect of the oxygen will become constant throughout an experiment and the reaction will now follow a first order equation. Data for typical runs in the presence of a large amount of added oxygen are given in Table IV, and the results of a number of such runs are given in Fig. 3 in the form of a $\ln \frac{a}{a-x} - t$ plot.

It will be seen that quite good first order constants are obtained. We may therefore conclude that added oxygen retards the reaction in the same way as does oxygen formed in it. Whether added oxygen is as efficient as

TABLE IV

TYPICAL EXPERIMENTS WITH LARGE AMOUNTS OF ADDED OXYGEN

Initial N_2O pressure							
8.31 cm.				7.38 cm.			
Initial O_2 pressure							
32.24 cm.				27.92 cm.			
Time, min.	P, cm.	x, cm.	K_m	Time, min.	P, cm.	x, cm.	K_m
0	40.55	—	—	0	35.30	—	—
1	40.65	0.22	0.0117	1	35.45	0.33	0.0199
2	40.72	0.37	0.0099	2	35.56	0.57	0.0175
3	40.80	0.55	0.0099	3	35.66	0.79	0.0164
5	41.00	0.99	0.0110	5	35.85	1.21	0.0156
7	41.18	1.39	0.0113	7	36.04	1.63	0.1054
10	41.46	2.00	0.0119	10	36.33	2.27	0.0159
12	41.65	2.42	0.0124	15	36.68	3.04	0.0154
14	41.82	2.79	0.0127	20	36.92	3.56	0.0143
16	41.96	3.10	0.0128	25	37.14	4.05	0.0138
20	42.28	3.81	0.0133	30	37.38	4.58	0.0140
24	42.48	4.25	0.0129	40	37.64	5.15	0.0130
30	42.72	4.77	0.0123				
50	43.40	6.27	0.0122				
70	43.70	6.93	0.0117				

that formed in the reaction in causing its retardation still requires investigation. In order to test this point runs were made with successively smaller amounts of added oxygen. Fig. 3 also shows the results of two runs with a 1 to 1 oxygen-nitrous oxide mixture, and the data for two typical runs of this type are given in Table V.

It will be seen from Table V that, while there is a certain amount of drift of the constants, the reaction is still virtually first order, the added oxygen being still sufficient to swamp out the effect of the oxygen formed in the reaction. Experiments were therefore made with very small amounts of added oxygen, and the results are given in Table VI for two typical cases. It will be seen that the reaction is no longer even approximately first order. A $K_m - V$ plot of these runs is given in Fig. 4, from which it may be seen that the linearity is excellent.

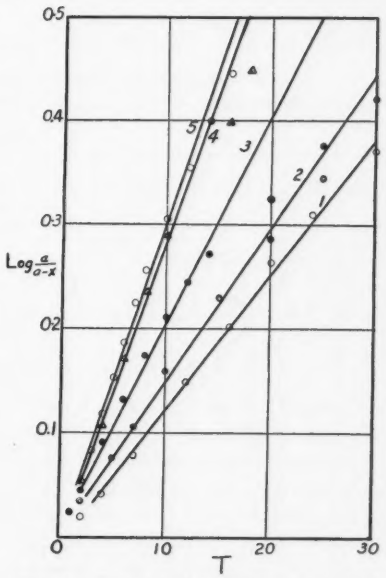

FIG. 3. *Experiments with large amounts of added oxygen. Curves 1, 2, and 3 for runs with a 4 O_2 : 1 N_2O mixture. Curves 4 and 5 for runs with a 1 O_2 : 1 N_2O mixture.*

TABLE V

EXPERIMENTS WITH APPROXIMATELY 1 : 1 N_2O — O_2 MIXTURES

Initial N_2O pressure							
8.27 cm.				5.85 cm.			
Initial O_2 pressure							
8.83 cm.				6.25 cm.			
Time, min.	P, cm.	x, cm.	K_m	Time, min.	P, cm.	x, cm.	K_m
0	17.10	—	—	0	12.10	—	—
1	17.34	0.53	0.0288	1	12.38	0.62	0.0487
2	17.54	0.97	0.0271	2	12.60	1.10	0.0452
3	17.74	1.41	0.0271	3	12.85	1.65	0.0480
4	18.00	1.98	0.0297	4	13.04	2.08	0.0499
6	18.42	2.90	0.0312	5	13.26	2.55	0.0497
8	18.76	3.65	0.0316	6	13.44	2.95	0.0508
10	19.00	4.18	0.0306	8	13.72	3.56	0.0509
12	19.20	4.62	0.0296	10	13.90	3.96	0.0491
14	19.36	4.97	0.0285	14	14.16	4.53	0.0465
18	19.66	5.63	0.0276	18	14.38	5.02	0.0471
22	19.90	6.16	0.0270	25	14.56	5.46	0.0470
26	20.09	6.58	0.0269				
35	20.40	7.04	0.0237				

TABLE VI

EXPERIMENTS WITH SMALL AMOUNTS OF ADDED OXYGEN

Initial N_2O pressure								
20.51 cm.					9.20 cm.			
Initial O_2 pressure								
5.34 cm.					2.40 cm.			
Time, min.	P, cm.	x, cm	K_m	V	P, cm.	x, cm.	K_m	V
0	25.85	—	—	—	11.60	—	—	—
0.5	26.70	1.87	0.0832	3.74	12.12	1.14	0.1150	2.28
1	27.45	3.52	0.0818	3.52	12.62	2.24	0.1212	2.24
1.5	28.10	4.95	0.0800	3.30	13.00	3.08	0.1180	2.05
2	28.65	6.16	0.0776	3.08	13.28	3.70	0.1117	1.85
3	29.70	8.47	0.0771	2.82	13.70	4.62	0.0976	1.54
4	30.44	10.10	0.0721	2.52	14.08	5.46	0.0977	1.36
5	31.02	11.37	0.0701	2.27	14.36	6.07	0.0936	1.21
6	31.50	12.43	0.0674	2.07	14.56	6.51	0.0890	1.08
8	32.24	14.06	0.0628	1.75	14.85	7.15	0.0815	0.89
10	32.74	15.16	0.0584	1.52	15.04	7.57	0.0752	0.76
12	33.12	15.99	0.0547	1.33	15.14	7.79	0.0679	0.65
14	33.36	16.52	0.0508	1.17	15.24	8.01	0.0634	0.57
18	33.76	17.40	0.0455	0.97	15.32	8.18	0.0531	0.45
22	33.98	17.89	0.0406	0.81	—	—	—	—
30	34.18	18.33	0.0324	0.61	15.46	8.49	0.0371	0.28

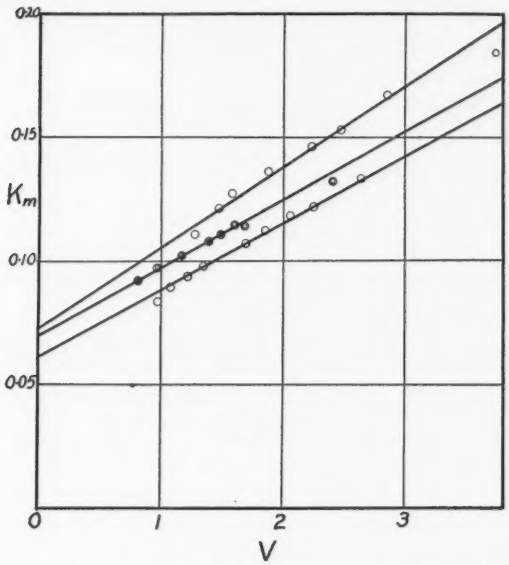

FIG. 4. *Experiments with small amounts of added oxygen.*

If y is the concentration of added oxygen, the other symbols having the same meaning as before, the rate equation becomes

$$\frac{dx}{dt} = \frac{K(a - x)}{1 + b(x + 2y)} ,$$

which on integration gives

$$\frac{(1 + 2by + ab)}{t} \ln \frac{a}{a - x} - \frac{bx}{t} = K .$$

Whence

$$V = (a + 2y + 1/b)K_m - K/b .$$

Hence V should be a linear function of K_m, the intercept being $-K/b$ as before. The slope, however, is now $(a + 2y + 1/b)$ instead of $(a + 1/b)$. Fig. 4 shows that K_m plotted against V gives straight lines.

Unfortunately the runs in Table VI and Fig. 4 are not strictly comparable with the preceding runs, inasmuch as they were done with a new catalyst, the former one having been accidently damaged. Experiments showed that the new catalyst had an activity about 1.80 times greater than the former (*i.e.* K was 1.80 times larger, *viz.*, 0.69), but that the constant b was unchanged. Thus for a number of runs with pure nitrous oxide with the new catalyst, using $K = 0.69$, and the previous value of b, we have

P, cm.	7.9	10.7	30.0	10.1	19.6
t_{50}, obs.	2.2	2.2	5.1	2.2	3.0
t_{50}, calcd.	2.1	2.5	5.0	2.4	3.3

The simplest way of checking the efficiency of the added oxygen in retarding the reaction is to calculate t_{50} and compare the result with experiment. In the presence of added oxygen we have

$$t_{50} = \frac{0.69}{K} + \frac{0.19ab}{K} + \frac{2 \times 0.69by}{K} .$$

Hence for the new catalyst we have

$$t_{50} = 1 + 0.138a + 1.0y ,$$

and for the old

$$t_{50} = 1.8 + 0.252a + 1.8y .$$

Whence for the experiments listed in Tables IV, V, and VI we have

Experiment	Table IV	Table V	Table VI
t_{50}, obs.	22.5, 22.0	10.0, 6.0	4.2, 3.0
t_{50}, calcd.	62.1, 53.8	19.8, 14.6	9.2, 4.7

Of course, on account of the unavoidable fluctuations in activity which occur in all catalytic investigations, a very close agreement between the observed and calculated values of t_{50} is hardly to be expected. There is, however, no doubt that the observed values of t_{50} in the presence of added oxygen are considerably lower than those calculated. In other words, added oxygen is not as efficient in retarding the reaction as is that formed in it, by a factor of 2 or 3. Inasmuch as oxygen formed in the reaction is adsorbed at the moment of its formation, it is evident that a slight time lag before desorption could cause temporary supersaturation of the surface and explain the observed effect. Such a time lag is, in fact, to be expected.

It may therefore be concluded that added oxygen affects the rate in the manner indicated by the rate equation, but is not quite as efficient as oxygen formed in the reaction. There are, however, no peculiarities of the type observed in the decomposition on a platinum catalyst.

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STUDIES ON HOMOGENEOUS FIRST ORDER GAS REACTIONS

VII. THE DECOMPOSITION OF ETHYLIDENE DIBUTYRATE AND HEPTYLIDENE DIACETATE[1]

By C. C. Coffin[2], J. R. Dacey[3] and N. A. D. Parlee[4]

Abstract

Ethylidene dibutyrate and heptylidene diacetate decompose in the vapor state at temperatures between 200° and 300° C. to form an aldehyde and an anhydride. The reactions are homogeneous, unimolecular, and complete. The activation energy is the same as that previously found for other members of this homologous series. Ethylidene dibutyrate decomposes at the same rate as ethylidene diacetate, and thus provides further evidence that the specific reaction velocity is independent of the size of the anhydride radicals. Heptylidene diacetate decomposes at the same rate as butylidene diacetate. This indicates that after the aldehyde radical has attained a certain size (three or four carbon atoms) the addition of $-CH_2-$ groups leaves the specific reaction velocity unchanged. The velocity constants are given by the equations

$$\text{ethylidene dibutyrate, } k = 1.8 \times 10^{10} e^{-\frac{33000}{RT}},$$

$$\text{heptylidene diacetate, } k = 3.0 \times 10^{10} e^{-\frac{33000}{RT}}.$$

Introduction

A study of the thermal decomposition of ethylidene diacetate homologues has been undertaken for reasons already outlined (1, 4, 5). This paper is concerned with the breakup of ethylidene dibutyrate and heptylidene diacetate —the largest purely aliphatic molecules of this series yet investigated. These esters resemble their homologues in that their vapor phase decomposition is unimolecular and homogeneous, and goes to completion at pressures up to atmospheric. Within experimental error, the activation energies are identical with those found for other members of the series. Ethylidene dibutyrate at any temperature decomposes at the same rate as ethylidene diacetate. The specific reaction velocity of heptylidene diacetate is somewhat greater than this, and is practically the same as that of butylidene diacetate. These data are thus further evidence that additions to the anhydride side of the molecule are without influence on the decomposition velocity. It appears also that after the butylidene radical is reached, no velocity increment accompanies the addition of $-CH_2-$ groups to the aldehyde side. In this respect the chemical behavior parallels the well known tendency of many physical properties to reach the limiting value of the series with the four carbon member.

It is worth emphasizing that the reaction is of such a type and occurs over such a temperature range that the observed rate is almost certainly that of the primary unimolecular step.

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Experimental

Preparation of Esters

The esters were prepared by heating equimolecular quantities of the respective aldehydes and anhydrides in the presence of a trace of sulphuric acid. The products were washed with sodium acetate solution, dried with calcium chloride, and fractionated by vacuum distillation. Their identity and purity were established by saponifications and molecular weight determinations.

Rate Measurements

Two independent pieces of apparatus (volumes of reaction chambers were 1020 and 384 cc.) of a type already described (3) were used for most of the reaction velocity measurements. For each ester the pressure increase was quite accurately 100%. In a few experiments carried out in bulbs the percentage reaction in a known time at a known temperature was determined by analysis of the reaction products.

Results

The experimental results are summarized in Table I. The initial pressures given in Column 3 are calculated by means of the gas laws from the weight

TABLE I

SUMMARY OF REACTION VELOCITY DATA

Run No.	$T°$, Abs.	P_o, cm. Hg.	$k \times 10^4$ (sec.$^{-1}$)	$-\log k$	$1/T$
Ethylidene dibutyrate					
15	513.0	9.0	1.27		
16	513.0	8.7	1.40		
22	513.1		1.50		
23	513.1		1.10	3.839	0.001949
24	513.1		1.50		
25	513.1		1.00		
27	512.9		2.25		
1	515.2	8.9	1.71	3.768	0.001941
2	515.2	13.6	1.70		
5	495.2	3.3			
8	494.4	18.2	0.451	4.346	0.002022
10	526.8	10.1	4.44		
11	526.8	10.2	4.50		
12	526.8	10.9	4.06	3.363	0.001898
13	526.9	12.2	4.32		
14	526.9	10.9	4.36		
3	539.3	9.7	9.35		
4	539.3	3.6	7.51	3.060	0.001855
6	539.3	10.3	9.34		
7	539.3	2.7	8.70		
17	563.0	27.3	27.0	2.585	0.001776
18	563.2	14.4	25.0		
19	533.2	35.7	6.80		
20	533.3	19.1	5.90	3.171	0.001876
21	533.3	35.8	7.00		
26	533.0	34.0	7.28		

TABLE I—*Concluded*

SUMMARY OF REACTION VELOCITY DATA—*Concluded*

Run No.	$T°$, Abs.	P_o, cm. Hg.	$k \times 10^4$ (sec.$^{-1}$)	$-\log k$	$1/T$
Heptylidene diacetate					
3	503.0	18.5	1.44	3.873	0.001987
14	503.2	32.0	1.50		
15	503.3	8.8	1.39		
12	513.0	21.9	2.24	3.616	0.001949
13	513.0	13.4	2.53		
24	512.7	16.9	2.50		
10	523.1	25.6	4.94	3.311	0.001912
11	523.1	11.7	4.90		
1	523.0	23.0	4.84		
9	533.0	21.2	8.91	3.048	0.001874
8	532.7	27.5	8.37		
23	533.1	18.4	9.5		
21	533.2	34.4	9.06		
7	543.0	27.1	17.4	2.775	0.001842
6	542.9	23.3	17.0		
18	543.1	13.0	16.8		
19	543.1	23.4	16.6		
5	553.0	31.6	24.6	2.554	0.001808
4	552.9	26.6	27.6		
25	553.0	30.2	31.4		
16	563.2	44.7	55.1	2.260	0.001776
17	563.0	39.2	59.5		
20	563.1	13.3	45.0		
22	562.6	25.7	60.0		

of ester taken. These values were usually found to be within a few millimetres of those obtained by extrapolating the observed pressures to zero time, and to be equal, within experimental error, to one-half the final pressure. It is true that the experimental error is greater than usual on account of the fact that the low volatility of these esters necessitates a relatively high pressure of mercury vapor in the reaction chamber.

The velocity constants (Column 4) were calculated by either the Guggenheim method (6), or by plotting $\log P_o/(2P_o - P)$ against time (1).

The average value of $-\log k$ (Column 5) at each temperature is plotted against $1/T$ in Fig. 1 which, for the sake of comparison, includes the previously published data for ethylidene diacetate (1) and butylidene diacetate (2). The broken line represents the decomposition of methylene diacetate (5).

It is evident from Fig. 1 that, as far as it can be decided from these experiments, each ester has an activation energy of about 33,000 cal. per mole. It must be admitted that a more intensive study may reveal differences in

activation energies of sufficient magnitude to account for at least some of the observed differences in reaction rates. However, it is tentatively assumed that the exponential factor in the rate equation is a constant for this series of compounds. Such an assumption appears to be not unreasonable (see (9, p. 50)) and facilitates considerably a systematic presentation of the data.

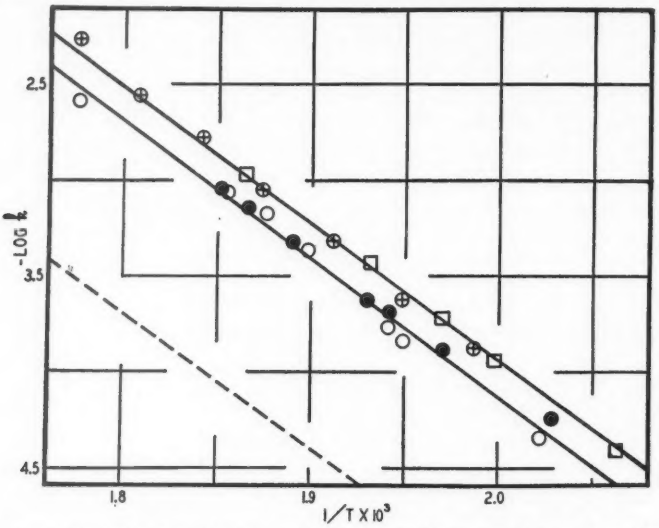

FIG. 1. *—log k plotted against* $1/T$. ○, *Ethylidene dibutyrate;* ●, *ethylidene diacetate;* ⊕, *heptylidene diacetate;* □, *butylidene diacetate:* - - - -, *methylene diacetate.*

As already pointed out there is a marked difference between the reaction rates of the methylene and the ethylidene esters. The difference between those of ethylidene diacetate and butylidene diacetate is small, but it is in the same direction and is probably real. The butylidene and heptylidene compounds, however, react at the same rate at all temperatures. The ethylidene diacetate and ethylidene dibutyrate decompositions are also indistinguishable as regards rate and temperature coefficient.

Velocity constants are given by the equations:

$$\text{Ethylidene dibutyrate, } k = 1.8 \times 10^{10}\, e^{-\frac{33000}{RT}},$$

$$\text{Heptylidene diacetate, } k = 3.0 \times 10^{10}\, e^{-\frac{33000}{RT}}.$$

In the case of several of these esters a special effort was made to obtain a few accurate measurements under as nearly identical conditions as possible, and to discover and eliminate any catalyst that might be present. It was thought that the obscurity introduced by the uncertainty in the exponential factor of the rate expression might be avoided by such a direct comparison of the reactions at one temperature. The esters chosen were ethylidene diacetate, ethylidene dibutyrate, and butylidene diacetate. About 300 gm. of each

compound (already "purified" for reaction rate measurements) was carefully fractionated *in vacuo* through a well packed and insulated 2-ft. column. The first 5 cc. and the last 5 cc. of the distillates were collected separately, and were used for the comparative runs summarized in Table II. These runs were carried out at 253.7° C. in the large reaction chamber (volume, 1020 cc.), and every effort was made to keep conditions constant and obtain accurate readings. The temperature was unfortunately somewhat too high for the breakup of butylidene diacetate (the half-life at 253.7° C. is about 14 min.) to be followed with accuracy in this type of apparatus.

TABLE II

RATE OF DECOMPOSITION OF ETHYLIDENE DIACETATE, ETHYLIDENE DIBUTYRATE, AND BUTYLIDENE DIACETATE AT 253.7° C.

——	Fraction	P_o, cm.	$k \times 10^4$
Ethylidene diacetate	First	17.55	4.76
	First	16.50	4.27
	Last	13.10	4.95
	Last	14.43	4.50
		Mean	4.62
		Calculated from rate equation	4.68
Ethylidene dibutyrate	First	11.13	4.24
	First	10.94	4.36
	Last	10.24	4.50
	Last	12.25	4.32
		Mean	4.36
		Calculated from rate equation	3.89
Butylidene diacetate	First	16.25	9.5
	First	15.37	8.1
	Last	12.29	9.3
	Last	14.45	8.7
		Mean	8.9
		Calculated from rate equation	7.4

It is evident from Table II that no catalyst has been concentrated in either the first or last fractions of any of the esters, so that there can be little doubt that the observed variation of the velocity constant with molecular structure is real. The agreement between the observed constants and those calculated from the previously published rate equations for ethylidene diacetate and butylidene diacetate is quite satisfactory. This indicates that the uncertainty in the activation energy is not much greater than that in determining the absolute rate. The importance of this is that the ethylidene esters have almost the same decomposition velocity, which is appreciably smaller than that of the butylidene compound.

The homogeneity of the reactions was established by experiments in which the esters were decomposed in bulbs packed with pieces of glass tubing. After a definite time in the thermostat, the contents of the bulbs was washed out and titrated with standard alkali. Changing the surface-volume ratio from 0.5 to 15 cm.$^{-1}$ caused no noticeable increase in the reaction rate.

It is of interest also that these esters decompose at the same rate in the liquid as they do in the vapor phase. For example, the values of $k \times 10^5$ found for liquid butylidene diacetate at 210° C. were 3.5 (two hours) 2.9 (four hours) and 3.0 (six hours). The value calculated from the rate equation of the vapor phase reaction is 3.3. These liquid phase decompositions will be dealt with in a later paper.

Discussion

The main features of these ester decompositions may be briefly summarized. It is evident that the activation energy remains essentially constant throughout the series, so that the differences observed in the reaction velocities are probably due to variations in the non-exponential factor of the rate expression. Such behavior seems to be characteristic of homologous series, which decompose by a clean-cut first order mechanism (9, 10).

The effect of structural changes on the specific reaction rate is noteworthy. There is no appreciable difference between the decomposition velocities of the diacetates and the dibutyrates, so that it seems that the addition of $-CH_2-$ groups to the anhydride radicals has little or no effect on the rate of reaction. The relative specific reaction velocities of the methylene, ethylidene, and butylidene esters at any temperature are respectively 1, 12 and 18; that is, the addition of a $-CH_2-$ group to the aldehyde radical is accompanied by a rate increase that diminishes as the series is ascended. The fact that there is no appreciable difference between the decomposition velocities of the butylidene and heptylidene esters indicates that this effect becomes negligible after the radical has acquired more than three or four $-CH_2-$ groups. There is thus a noteworthy difference between this series and the alkyl nitrites, in which the rate approximately doubles for each added $-CH_2-$ group (10).

As existing theories do not take into account the quantitative details of complex dissociations, the mechanism underlying even such apparently consistent trends can only be guessed at. It seems probable, however, that the observed differences in specific reaction velocities are due to differences in the proportionality factors (the A factors) of the rate expressions, so that the problem becomes one of correlating changes in A with changes in molecular structure. It has already been suggested (2, 4) that the existence of intramolecular "insulators" might limit the number of vibrational degrees of freedom in communication with the potentially reactive bonds, so that the rate of internal energy distribution, and hence the value of A, would depend to a certain extent on the structure of the molecule. In the case of the ethylidene diacetate homologues, for example, it may be that the aldehyde radical exchanges energy with the reacting bonds more easily than do the anhydride radicals. The fact that the effectiveness of an added $-CH_2-$ group decreases as its distance from the breaking bond increases, may mean that the latter can acquire energy from only those degrees of freedom in its immediate neighborhood. In principle, at least, such a mechanism appears to be not unlikely. It is indeed essentially the mechanism adopted by Hinshelwood to explain the segmented rate-pressure curves sometimes found for the low pressure decomposition of molecules of intermediate complexity (7:8, p. 215).

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STUDIES ON HOMOGENEOUS FIRST ORDER GAS REACTIONS

VIII. THE DECOMPOSITION OF TRICHLORETHYLIDENE DIACETATE AND TRICHLORETHYLIDENE DIBUTYRATE[1]

By N. A. D. Parlee[2], J. R. Dacey[3] and C. C. Coffin[4]

Abstract

Trichlorethylidene diacetate and trichlorethylidene dibutyrate have been found to decompose at temperatures between 200° and 290° C. at a measurable rate to give chloral and an acid anhydride. The reactions are homogeneous and of the first order, and have the same specific velocity in both the liquid and vapor states. The activation energy is identical (within experimental error) with that previously found for non-chlorinated members of this series of esters. The two compounds decompose at the same rate, in agreement with the hypothesis that the anhydride radicals do not easily exchange energy with the bonds that break. This reaction velocity, which is somewhat smaller than that of ethylidene diacetate at any temperature, is given by the equation $k = 1.3 \times 10^{10} e^{-\frac{33000}{RT}}$.

Introduction

It has been shown in previous papers (for references see (3)) that the decomposition velocities of esters made from an aldehyde and an acid anhydride are sensitive to structural changes on the "aldehyde end" of the molecule. The specific reaction rate at any temperature tends to increase with the number of $-CH_2-$ groups in the aldehyde from which the ester is made. Increasing the size of the anhydride has little or no effect on the velocity of decomposition. The activation energy appears to be independent of all such structural changes. It is of interest to investigate the effect of varying the kind as well as the number of atoms in the different radicals on the activation energy and the reaction velocity.

The present paper deals with the decomposition of trichlorethylidene diacetate and trichlorethylidene dibutyrate—esters made by the addition of chloral to the respective anhydrides. These compounds have been found to behave very much like other non-chlorinated members of the series. Their decomposition is homogeneous and unimolecular, and proceeds at the same rate in both the liquid and gaseous states. They have the same decomposition velocity, which is somewhat smaller than that of ethylidene diacetate The activation energy is the same as that of other members of the series.

Experimental

Preparation of the Esters

The esters were prepared by adding freshly distilled chloral to an equivalent quantity of the acid anhydride. A trace of sulphuric acid was used as a catalyst. After the product was washed with a solution of sodium acetate it was purified by fractional distillation *in vacuo*. A good yield of very pure

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ester is readily obtained. At atmospheric pressure the boiling points of the diacetate and the dibutyrate are about 225° and 247° C. respectively. Two independent preparations of the diacetate were used in the reaction velocity measurements.

Rate Measurements

The gas reaction was followed by the rate of pressure increase at constant volume in an apparatus of a type already described (2). Two reaction chambers (volumes, 307 and 348 cc.) were used in the experiments listed in Table I. In each case less than 1% of the total volume was below the temperature of the mercury vapor jacket. Temperatures were determined from the vapor pressure curve of mercury. The rates of decomposition were found to be independent of the partial pressure of mercury in the reaction chamber.

The velocity of the reaction in the liquid state was determined by an analytical method. Sealed tubes almost filled with an ester (0.5 to 1.0 gm.) were kept at a known temperature for a known time. The contents were then washed into water free from carbon dioxide, and, after the anhydride had changed to acid, were titrated with 0.1 *N* barium hydroxide. The bulbs were weighed before and after emptying. Vapor thermostats at 210° (nitrobenzene) and 223° C. (methyl salicylate) were used.

Results

The data on the velocity of the gas reactions are given in Table I. The initial pressures (Column 3) are calculated by means of the ideal gas laws from the weight of ester taken. These values were always found to agree

TABLE I

REACTION VELOCITIES IN THE VAPOR PHASE

Run No.	T°, Abs.	P_o, cm. Hg.	$k \times 10^4$ (sec.$^{-1}$)	$-\log k$	$1/T$
Trichlorethylidene diacetate					
10	503.0	26.5	0.55	4.268	0.001987
11	503.0	54.7	0.60		
28	503.5	26.3	0.48		
1	513.0	28.1	1.11	3.955	0.001949
29	513.0	20.0	1.19		
2	523.0	32.4	1.64	3.731	0.001912
3	523.0	36.3	1.68		
4	523.0	33.0	1.71		
20	523.1	18.3	1.92		
21	523.0	17.4	2.09		
22	523.3	28.2	2.11		
6	533.0	28.9	3.56	3.458	0.001874
7	532.7	39.0	3.15		
8	532.9	16.0	3.46		
9	532.9	30.0	3.57		
23	533.4	17.2	3.51		
24	533.0	31.7	3.11		
25	533.2	22.5	3.76		
26	532.8	20.3	3.76		

TABLE I—*Concluded*

REACTION VELOCITIES IN THE VAPOR PHASE—*Concluded*

Run No.	T°, Abs.	P_o, cm. Hg.	$k \times 10^4$ (sec.$^{-1}$)	$-\log k$	$1/T$
Trichlorethylidene diacetate—Concluded					
12	542.0	22.0	6.37	3.188	0.001841
13	543.0	27.3	6.55		
27	543.0	21.8	6.53		
30	543.0	23.7	6.45		
14	553.0	36.2	12.3	2.909	0.001808
15	553.0	24.0	12.4		
16	553.0	16.0	12.3		
17	553.0	5.0			
31	563.0	26.8	21.3	2.680	0.001776
32	562.9	8.9	20.5		
Trichlorethylidene dibutyrate					
13	514.1	5.3	1.2	3.839	0.001947
20	513.0	21.3	1.7		
11	522.7	7.8	1.97	3.688	0.001912
12	523.2	11.5	2.14		
7	533.0	14.4	4.43	3.369	0.001876
8	532.9	12.7	4.51		
15	533.2	11.4	3.9		
5	543.1	15.1	8.58	3.058	0.001842
6	542.9	15.4	8.15		
9	543.0	14.3	8.28		
16	543.1	9.3	10.0		
21	543.0	25.3	8.7		
3	552.9	21.6	13.2	2.854	0.001808
4	553.0	15.6	14.0		
19	552.9	22.1	15.1		
22	553.0	21.2	13.7		
1	563.1	18.8	23.1	2.613	0.001776
10	562.9	20.4	26.9		
18	562.9	24.2	23.1		

within several millimetres with that obtained by extrapolating the observed pressures (corrected for the partial pressure of mercury vapor and the difference in temperature of the two sides of the manometer) to zero time. Within the limits of error of the extrapolation, the initial pressure was always found to be one-half the final pressure in spite of the fact that a secondary reaction caused a slow but steady drift in the latter. This increase, which amounts to 2 or 3% in 24 hr. at any temperature, is easily corrected for. It is probably due to a heterogeneous polymerization and decomposition of chloral on the chamber walls, which become more and more thickly coated with a brown lacquer-like film.

The majority of the first order velocity constants listed in Column 4 were calculated by the Guggenheim method (4). In cases where it was not convenient to take readings at equal time intervals, $\log \frac{P_o}{2P_o - P}$ was plotted against time, and the velocity constant was obtained from the slope of the resulting straight line. The agreement between the two methods was in general very satisfactory. The data of a typical run (trichlorethylidene diacetate, No. 16) worked up by both methods are plotted in Fig. 1. It is evident that the reaction is strictly first order, and that no appreciable error is introduced by the uncertainty in the initial and final pressures.

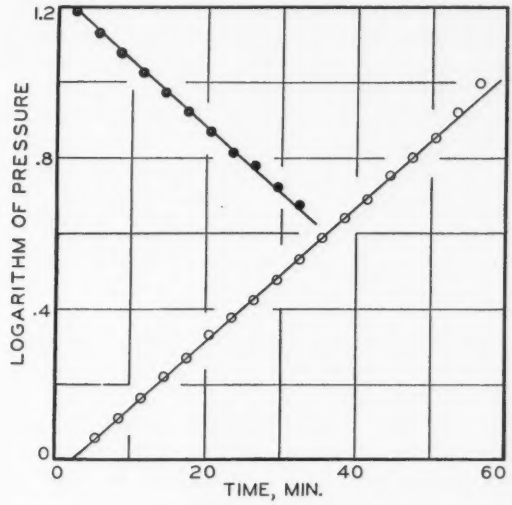

FIG. 1. *Data of a typical run.* ●, *Guggenheim method;* ○, $\log \frac{P_o}{2P_o - P}$.

The values obtained for the reaction rates in the liquid state are summarized in Table II. The percentage reaction given in Column 4 is the mean of two determinations carried through in duplicate. These usually agreed within about 2%. The contents of the bulbs gradually became dark red at the reaction temperature. If left in the thermostat for a long time (decomposition = 80–90%), the reaction mixture became badly charred, and a high pressure of permanent gas developed. This secondary reaction is believed to be the decomposition of chloral or of one of its polymers, as it does not occur in the case of some esters made from the same anhydrides and other aldehydes.

The quite satisfactory agreement between the first order velocity constants (uncorrected for any reverse reaction) found for different reaction times indicates that the decomposition in the liquid state is unimolecular and that it goes to completion. This reaction in the pure liquid state and in solution is being more fully investigated.

TABLE II

DECOMPOSITION IN THE LIQUID STATE

Bulb No.	Temp., °Abs.	Time, hr.	Reaction, %	$k \times 10^5$	$-\log k$ (mean)	$1/T$ (mean)
Trichlorethylidene diacetate						
1, 2	483.2	4.6	25.3	1.77		
3, 4	483.6	2.0	11.2	1.79		
5, 6	483.6	5.0	26.4	1.70	4.765	0.002068
7, 8	483.6	16.0*				
9, 10	483.6	2.8	15.3	1.63		
11, 12	496.4	4.0	58.5	6.1		
13, 14	496.3	1.0	15.8	4.8		
15, 16	496.3	2.5	36.2	5.0	4.339	0.002010
17, 18	496.3	5.0*	89.7			
19, 20	496.3	1.5	24.4	5.2		
Trichlorethylidene dibutyrate						
1, 2	483.4	4.0	20.0	1.55		
3, 4	483.1	5.0	23.7	1.51	4.815	0.002070
5, 6	482.9	7.2	32.8	1.54		
7, 8	495.5	1.0	17.4	5.3		
9, 10	495.4	2.0	24.2	3.8	4.347	0.002018

* *Charred.*

The mean negative logarithms of the velocity constants and the mean reciprocal temperatures (Columns 5 and 6, Table I; 6 and 7, Table II) are plotted against each other in Fig. 2.

It is evident from Fig. 2 that the two compounds decompose at practically the same rate at all temperatures and that this is the same in both the liquid and gaseous states. It is true that on the average the dibutyrate

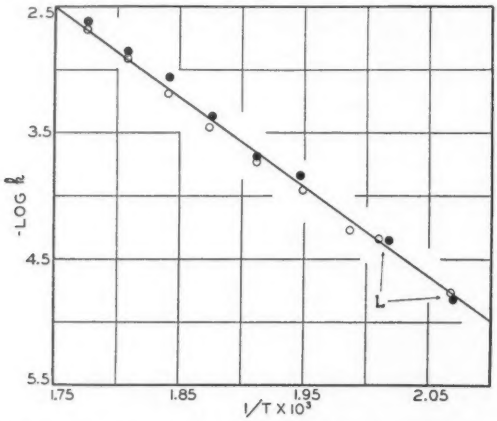

FIG. 2. —*Log k plotted against* $1/T$. ○, *Trichlorethylidene diacetate;* ●, *trichlorethylidene dibutyrate; L, indicates experiments in liquid state.*

points appear to be slightly higher than those of the diacetate. However, as the difference is probably within the limit of error of the present experiments, the two compounds may be tentatively regarded as decomposing at the same rate. This rate at any temperature is given by the equation (that of the straight line in Fig. 2)

$$k = 1.3 \times 10^{10} e^{-\frac{33000}{RT}}.$$

The decomposition velocity of ethylidene diacetate is given by the equation $k = 2.0 \times 10^{10} e^{-\frac{33000}{RT}}$. It is evident that within the accuracy of the data the trichlor-esters have the same activation energy as the other members of the series.

The fact that the activation energy is unchanged and that the A factor (*cf.* the equation $k = A e^{-\frac{E}{RT}}$) is changed only slightly by the substitution of three chlorine for three hydrogen atoms, is of considerable interest. It is remarkable that the stability of a bond (as measured by the energy necessary to break it) should be unaffected by weighting a neighboring atom so heavily. One might also expect that the specific reaction rate would undergo a greater change, particularly since the substitution is made in the only radical whose structure has been found to influence the rate (3). Other substitutions and structures are being investigated.

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STUDIES ON HOMOGENEOUS FIRST ORDER GAS REACTIONS

IX. THE DECOMPOSITION OF FURFURYLIDENE DIACETATE AND CROTONYLIDENE DIACETATE[1]

By J. R. Dacey[2] and C. C. Coffin[3]

Abstract

The vapor phase decomposition of furfurylidene diacetate and crotonylidene diacetate to acetic anhydride and their respective aldehydes is homogeneous, first order, and complete. The activation energy is that characteristic of the series, *viz.*, 33,000 cal. The specific reaction rates of the two esters are the same, and are about six times as great as that of ethylidene diacetate at any temperature. It is suggested that the increased velocity is due to the presence of the double bond. Velocity constants are given by the equation $k = 1.3 \times 10^{11} e^{-\frac{33000}{RT}}$.

Introduction

Previous papers of this series (3) have shown that the addition of $-CH_2-$ groups or chlorine atoms to ethylidene diacetate has little or no effect on the amount of energy required before the ester molecule decomposes into an aldehyde and an anhydride; that the influence of such structural alterations on the velocity of decomposition is not very large, and that it is apparently confined to the aldehyde end of the molecule. It is of interest to study the effect of more complex structural changes on the activation energy and reaction velocity.

The present paper deals with the breakup of furfurylidene diacetate and crotonylidene diacetate to acetic anhydride plus furfural and crotonaldehyde respectively. The former ester is characterized by a furan ring, the latter by a straight chain. Each has a double bond at the same distance from the point at which the molecules break. As is the case with other members of the series the vapor phase decomposition is homogeneous, unimolecular, and complete. Within experimental error the activation energy of each compound is that characteristic of the series. Their specific reaction velocities are identical, and are about six times as great as that of ethylidene diacetate and four times as great as that of butylidene diacetate at any temperature. It thus appears that the furan ring has no effect on the rate of the reaction or the stability of the molecule, and that the double bond is responsible for the observed velocity increase.

Experimental

The esters were prepared by refluxing the freshly distilled aldehydes with acetic anhydride containing a trace of sulphuric acid. They were purified and analyzed by methods already described (1, 3).

[1] *Manuscript received March 8, 1937.*
Contribution from the Laboratory of Physical Chemistry, Dalhousie University, Halifax, Canada.
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The reaction rate measurements were made in an improved apparatus (4). Velocity constants were calculated from the rate of pressure increase in the usual manner.

Results

The data are presented in Table I, which is self-explanatory.

TABLE I

SUMMARY OF REACTION VELOCITY DATA

Run No.	Temp., °Abs.	P_o, cm. Hg.	$k \times 10^3$, (sec.$^{-1}$)	$-\log k$	$1/T \times 10^3$
Furfurylidene diacetate					
21	493.1	18.8	0.326	3.507	2.028
22	493.1	33.6	0.297		
10	503.3	13.8	0.599	3.214	1.988
11	503.1	19.1	0.653		
12	503.1	2.0	0.650		
17	502.9	17.5	0.541		
6	513.1	18.1	1.14	2.963	1.949
8	513.1	12.2	1.15		
9	513.1	24.5	0.99		
1	523.0	52.1	2.03	2.701	1.912
2	523.0	39.9	2.01		
3	523.1	23.9	1.85		
4	522.9	10.4	2.04		
5	522.9	18.3	2.04		
13	532.7	16.2	3.03	2.434	1.877
15	532.8	33.0	4.05		
16	532.8	26.0	3.95		
18	542.9	17.5	7.26	2.148	1.842
19	542.9	41.6	6.85		
20	542.9	15.9	7.23		
23	553.0	23.0	13.4	1.917	1.808
25	552.9	19.1	11.3		
26	553.0		12.2		
27	553.0		12.3		
28	553.0	29.0	10.7		
29	553.0	7.2	13.0		
Crotonylidene diacetate					
4	492.0	42.1	0.379	3.456	2.032
5	492.1	12.3	0.331		
6	492.2	13.5	0.343		
7	503.7	34.1	0.615	3.199	1.986
8	503.5	19.7	0.655		
9	503.5	16.9	0.628		
1	513.0	26.4	0.97	2.943	1.952
10	511.9	30.7	1.32		

TABLE I.—*Continued*

SUMMARY OF REACTION VELOCITY DATA—*Continued*

Run No.	Temp., °Abs.	P_o, cm. Hg.	$k \times 10^3$, (sec.$^{-1}$)	$-\log k$	$1/T \times 10^3$
Crotonylidene diacetate—Concluded					
23	515.0	17.8	1.1	2.920	1.942
24	515.0	7.1	1.2		
25	515.0	4.4	1.4		
26	515.0	11.7	1.2		
11	522.6	21.2	2.23	2.631	1.914
12	522.2	26.9	2.29		
13	522.4	19.7	2.51		
14	533.3	24.6	4.04	2.411	1.875
15	533.1	51.3	3.52		
16	533.4	9.6	4.08		
22	539.0	27.7	4.8	2.32	1.855
17	543.2	19.5	7.10	2.167	1.841
18	543.2	23.5	6.33		
19	543.2	10.6	6.99		
20	533.2	7.7	13.8	1.900	1.808
21	533.2	18.7	12.0		
2	533.0	18.1	12.1		

In Fig. 1 the negative logarithms of the velocity constants (Column 5) are plotted against the reciprocals of the absolute temperatures. In order to conform with the previously adopted assumption (1, 2) that velocity differences are due to variations in the A factor of the rate equation, the

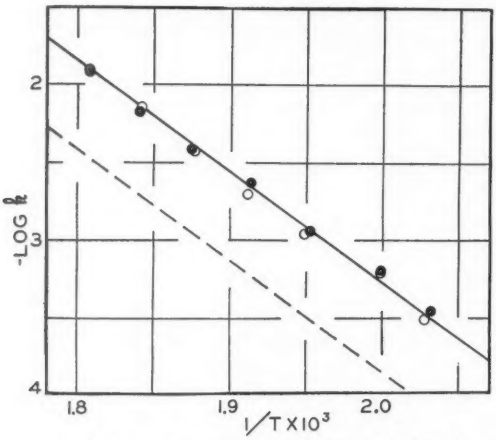

FIG. 1. —*Log k plotted against 1/T. Broken line, butylidene diacetate;* ○, *furfurylidene diacetate;* ●, *crotonylidene diacetate.*

straight line of Fig. 1 has been arbitrarily given a slope corresponding to an activation energy of 33,000 cal. It is obvious that the line fits the data within experimental error. For purposes of comparison the position of the butylidene diacetate line is indicated on the diagram. Velocity constants of the furfurylidene and crotonylidene diacetate decomposition are given by the equation $k = 1.3 \times 10^{11} e^{-\frac{33000}{RT}}$.

A comparison of the reaction rates and structural formulas of butylidene and crotonylidene diacetates at once suggests that the enhanced reactivity of the latter is due to the presence of the double bond. Moreover, unless the correspondence between the crotonylidene and furfurylidene velocities is entirely fortuitous, it would seem that the double bond is the only difference (as far as factors influencing reaction rate are concerned) between the butylidene and furfurylidene esters. Further discussion is reserved until more data have been collected.

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THE REACTION OF DEUTERIUM ATOMS WITH METHANE AT HIGH TEMPERATURES[1]

By E. W. R. Steacie[2]

Abstract

Using the Wood-Bonhoeffer method, an investigation has been made of the reaction of deuterium atoms with methane at temperatures up to 500° C. Owing to the difficulties involved in poisoning the walls to prevent atom recombination at high temperatures, the atom concentration was very variable. The results are therefore only approximate, but they serve to establish definitely the presence of a reaction at the temperatures under investigation, and enable the estimation of the activation energy of the reaction

$$D+CH_4 = CH_3D+H,$$

viz., 12.9 ±2 Kcal. This is in good agreement with values obtained in other investigations.

Introduction

In the past few years the kinetics of a number of reactions involving atomic deuterium has been investigated.* Investigations of this kind often permit conclusions to be drawn regarding the rates of other atomic processes, and such information is of great interest, especially in connection with recent speculations regarding the participation of free radicals in chemical processes.

The reactions of hydrogen and deuterium atoms with methane have been the subject of considerable investigation. Early experiments (1, 16) showed that methane was unique in that it alone of the hydrocarbons seemed to be without effect on atomic hydrogen, being unattacked by it, and causing no "catalysis" of the recombination of hydrogen atoms. Ethane catalyzes the recombination of hydrogen atoms but is not appreciably attacked, while all other hydrocarbons react readily. Geib and Harteck (7) confirmed the above results and showed that no reaction occurred up to 183° C. They therefore concluded that the reaction $CH_4+H = CH_3+H_2$ has an activation energy of at least 17 Kcal.

Taylor, Morikawa, and Benedict (14) investigated the reaction of methane with deuterium atoms produced by photosensitization with mercury. The resulting deuteromethanes were detected by infra-red spectroscopy. They reported considerable reaction from 40° to 300° C., and concluded that the activation energy of the process was very low, of the order of 5 Kcal. They assumed that the primary reaction was $CH_4+D = CH_3+HD$.

Geib and Steacie (8, 9) investigated the same reaction by the Wood-Bonhoeffer method. They found no detectable reaction of deuterium atoms with methane up to 100° C. This indicated that the activation energy of the exchange reaction is equal to or greater than 11 Kcal., in sharp contrast to the result of Taylor, Morikawa, and Benedict. Their investigation

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Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Canada, with financial assistance from the National Research Council of Canada.
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* *See K. H. Geib (6) for a comprehensive review.*

indicated (by analogy with the reaction of deuterium atoms with other substances) that the reaction concerned is probably the analogue of the ortho-para hydrogen conversion, *viz.*

$$CH_4+D = CH_3D+H,$$

rather than

$$CH_4+D = CH_3+HD.$$

In any case, the investigation sets a lower limit of 11 Kcal. for the activation energies of both reactions.

Farkas (3) made a few preliminary experiments on the thermal exchange reaction between deuterium and methane at temperatures in the neighborhood of 1000° K. He showed that the thermal reaction proceeds by an atomic mechanism similar to that of the ortho-para hydrogen conversion, *viz.*

$$D_2 = 2D$$
$$D+CH_4 = CH_3D+H. \quad (1)$$

His results indicate that the activation energy is in the neighborhood of 11 Kcal.

The mercury photosensitized reaction was reinvestigated by Steacie and Phillips (13). In agreement with the results of Farkas and of Geib and Steacie they found an activation energy of about 11.7 Kcal. for the exchange reaction. The reaction was also investigated by Farkas and Melville (5) over a wide range of temperature, and they found an activation energy of 13 Kcal. They concluded, as did Steacie and Phillips, that the reaction was the analogue of the ortho-para hydrogen conversion. They found, however, that at high temperatures the D-atom concentration fell off greatly, and they suggest that the atom-consuming step is the reaction

$$D+CH_4 = CH_3+HD. \quad (2)$$

On this basis we would expect a small amount of ethane formation to accompany the exchange reaction.

Since the submission of the present paper, a report of a further investigation of the mercury photosensitized reaction by Morikawa, Benedict, and Taylor (12) has appeared. From the collision yield at 100° C. they calculate an activation energy of 12.5 to 14 Kcal. for Reaction (1) in good agreement with Steacie and Phillips and with Farkas and Melville. The experimental value of the temperature coefficient is very low, however, and they conclude that the true mechanism is not that indicated by Reaction (1). They suggest that the reaction is largely

$$Hg^*+CH_4 = CH_3+H+Hg$$

followed by a rapid exchange of the methyl radical probably through the formation and decomposition of a quasi-molecule CH_3D^*. The fact that some ethane formation occurs is cited as evidence for the presence of methyl radicals. They discuss a large number of possible secondary reactions, and conclude that one cannot obtain much information about Reaction (1) by the photosensitization method.

It seems to the writer, however, that the loss of hydrogen atoms at high temperatures found by Farkas and Melville is a sufficient explanation of the low temperature coefficient of the reaction, and that the postulation of a complicated series of processes is unnecessary. It should be noted that the experimental results of Morikawa, Benedict, and Taylor are in good agreement with those of previous investigations, the discrepancy being primarily one of interpretation.

In a further paper Trenner, Morikawa, and Taylor (15) report an investigation by the Wood-Bonhoeffer method. They found no reaction from 25 to 208° C., from which they calculate a minimum activation energy of 15.6 Kcal, for the exchange reaction. From a single run at 310° C. they calculate the activation energy to be 18 Kcal. These values are considerably higher than those obtained by other workers. The discrepancy is partly due to the fact that they assume that the primary reaction is No. 2, followed by a rapid exchange of the methyl radical. Hence to get the rate of the first step they divide the observed rate by 3. If the primary reaction is really No. 1 as concluded by all other workers in the field, this division should not be performed, and their activation energy will be lowered by nearly 1 Kcal.

All these investigations of the deuterium atom reaction prove conclusively that the activation energy of the reaction $CH_4+H = CH_3+H_2$ must be about 12 to 13 Kcal. In his recent review Geib points out that further evidence of the stability of methane to attack by hydrogen atoms is indicated by the fact that methane is obtained as an end product in many H-atom reactions.

It appears, therefore, that the results obtained by photosensitization, thermal, and discharge tube methods present a consistent picture. It would, however, be highly advantageous to have the H-atom results at low temperatures extended so as to approach the high temperature thermal range, and thus complete the investigation of the whole scheme. This has been attempted in the present investigation. Although, owing to experimental difficulties, the results are only approximate, nevertheless they do serve to establish fairly definitely the activation energy of the reaction by the discharge tube method, and to show that the results of all methods of investigation are entirely consistent.

Experimental

For the reasons outlined above, and also for the investigation of other reactions, it would be very desirable to be able to extend the Wood-Bonhoeffer method to high temperatures. Apparently no previous attempt to do this has been made. The main difficulty in doing so is, of course, obvious. The successful operation of the method requires the prevention of too fast a recombination of hydrogen atoms on the walls of the apparatus. This can be done only by poisoning the walls, and such poisoning has been previously accomplished by running the tube wet, or by coating the walls with phosphoric acid, potassium chloride, or sulphuric acid. At high temperatures the use of a wet tube, or of sulphuric acid, is impossible.

In preliminary experiments a quartz reaction vessel was used, and attempts were made to poison it with phosphoric acid and with potassium chloride. It was found that, apart from any question of the efficacy of poisoning agents, quartz is not a suitable material. In the process of blowing the quartz apparatus a certain amount of devitrification is almost inevitable, and it was found to be virtually impossible to poison such devitrified spots even at temperatures of 100° to 200° C.

The apparatus was therefore rebuilt of Pyrex glass. With this apparatus it was found that potassium chloride was definitely unsuitable for poisoning purposes at high temperatures. Attempts to run the apparatus with a very thoroughly cleaned wall without poisoning were unsuccessful, as might have been expected. A wall coated with phosphoric acid was satisfactory up to about 300° C. Above this temperature the phosphoric acid first dehydrated, and finally the dry phosphorus pentoxide largely distilled out of the reaction vessel. By coating fairly heavily, heating to high temperatures for the minimum possible time, and using "wet" hydrogen, it was possible to obtain a fair amount of success with phosphoric acid up to 500° C.

To get the maximum possible atom concentration at high temperatures, the reaction vessel was moved as close as possible to the discharge (about 5 cm.), and the partial pressure of methane was made very low to prevent its blowing back into the discharge. A small amount of methane did nevertheless get into the discharge, and this raised the "blank" correction by 3% or so, but this was unavoidable.

Under these conditions it was possible to obtain high atom concentrations and reasonably reproducible results up to about 350° C. At 500° C. the atom concentration was still appreciable (about 2%), but was very variable (by a factor of 2 or 3). However, it was possible nevertheless to make approximate measurements up to this temperature.

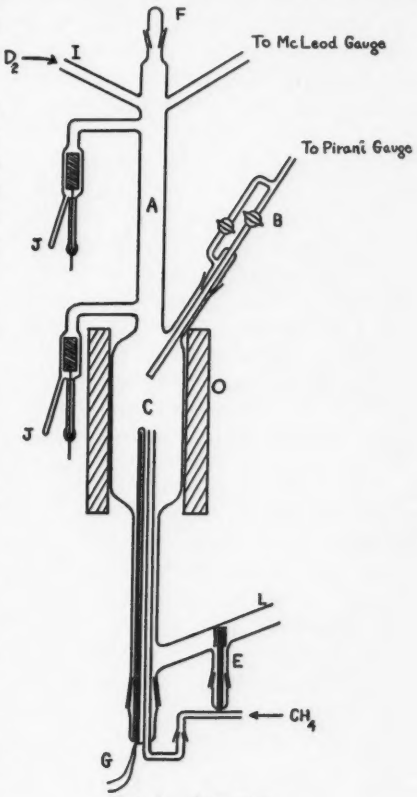

FIG. 1. *Apparatus.*

Apparatus

The main section of the apparatus is shown in Fig. 1. A discharge was run through the tube *A* (1 in.

diameter). The electrodes were aluminium cylinders attached to stout platinum leads which were taken out through a capillary tube sealed with deKhotinsky cement. The discharge was operated with an applied voltage of about 3500 across the tube and a 5000 ohm resistance. The voltage was varied with a step transformer and a rheostat in the primary so as to maintain a constant current of 340 milliamperes through the tube.

Below the discharge was a reaction vessel *C*, with a diameter of 7 cm. and a length of 40 cm. This was surrounded by an electric furnace *O*, which could be slipped up and down the tube so as to permit observation when the efficiency of the wall poisoning, etc., was tested. Two tubes entered the reaction vessel from below, one of which contained a thermocouple, and the other served as an inlet for methane.

The hydrogen atom concentration in the reaction vessel was measured with the Wrede gauge *B*. This was of the usual type (10, 17) and consisted of a tube *B* with a very fine orifice situated in the reaction vessel, and an arrangement of stopcocks such that either the inside of the tube or the outside could be connected to a Pirani gauge. On account of the difference in the diffusion coefficients of hydrogen atoms and hydrogen molecules, a pressure difference will be set up across the orifice, and this may be measured with the Pirani gauge. From the pressure difference the percentage of atoms in the vessel may be readily calculated. In addition, to serve as a rough check on the efficacy of the poisoning, etc., an ordinary mercury thermometer was placed at *E* with its bulb wrapped with platinum gauze and situated in the gas stream. A heating up to 50 or 60° C. could be obtained, and this gave a very rough measure of the atom concentration of the gas leaving the reaction vessel.

To facilitate poisoning the walls of the apparatus, the whole main section was made vertical as indicated. In order to wash the apparatus the ground cap *F* at the top, the inlet tubes and joint *G*, and the Wrede gauge *B* were removed. The tips were then cut off the small drainage tubes, *J*, attached to the electrodes. The apparatus was then washed out with distilled water, fuming nitric acid, water again, and finally with a 5% solution of phosphoric acid. The ground joints were then replaced, the tips of the tubes *J* sealed off, and the apparatus was dried by evacuation.

Deuterium was prepared in part by the electrolysis of alkaline 99.6% deuterium oxide, and in part by the reaction of 99.6% deuterium oxide with sodium. It was stored in a large bulb, and was pumped as required into a small mercury gas-holder by means of a Toepler pump. It then passed through a bubbler containing deuterium oxide, and a capillary flowmeter, and entered the apparatus at *I*. The flowmeter was adjusted so as to maintain the pressure in the apparatus at 0.30 mm.

Methane was secured in cylinders from the Ohio Chemical and Manufacturing Co. and was stated to be 96.5% methane. It was purified by fractional distillation and stored in a large reservoir. In making an experiment it was expanded into a small reservoir connected to the apparatus through a flowmeter. By adjusting the pressure in the small reservoir it was possible to secure any desired rate of flow.

After leaving the reaction vessel through the outlet tube L, the gas passed through a trap at liquid air temperature and a three stage steel mercury diffusion pump. This had a very high speed (approximately 20 litres per sec.) and could maintain a pressure of 0.30 mm. in the apparatus when deuterium was admitted at the rate of about 13 cc. at N.T.P. per minute. After leaving the diffusion pump the gas passed through a trap containing silica gel at $-180°$ C. to remove the methane, and then to a Hyvac pump.

At the end of an experiment, which normally lasted about 15 min., the silica gel trap was maintained at $-180°$ C. and pumped out for 5 min. with the Hyvac pump alone. Trials showed that it was possible to desorb virtually all adsorbed hydrogen in this way without appreciable loss of methane. The trap was then allowed to warm up to 0° C. to desorb the methane. The methane was then expanded into a two litre combustion pipette, dry oxygen was admitted, and the methane was burned on a platinum filament. The resulting water was freed from oxygen and carbon dioxide by repeated distillations at $-80°$ C. in a high vacuum. The water was then analyzed for its deuterium content by the thermal conductivity method of Harteck as described in previous papers.

Experimental Results

Atom Concentration

As was mentioned above, the deuterium atom concentration was measured with a Wrede diffusion gauge. In order to conserve deuterium, the atom concentration measurements were made in special calibration experiments using ordinary hydrogen. This introduces no appreciable error for the following reasons. If the pressure is kept the same, hydrogen will flow through the apparatus faster than deuterium and will take less time to get from the discharge to the reaction vessel. During this time, however, it will undergo more collisions on account of its higher molecular velocity. These two effects balance, and there will be no appreciable difference in the number of collisions undergone by hydrogen or by deuterium atoms (or molecules) while traveling between the discharge tube and the reaction vessel. Also, the activation energies of the recombination reactions

$$H+H(+M) = H_2(+M)$$

and

$$D+D(+M) = D_2(+M)$$

will not differ appreciably since atoms have no zero-point energy. Hence, we may expect the same atom concentration in the reaction vessel irrespective of whether hydrogen or deuterium is used. In any case, any possible error from this source is negligible compared to the uncertainties in the atom concentration on account of fluctuations in the activity of the walls.

At low temperatures the results were definitely reproducible and indicated an average of 36% atoms at 20° C. and 20% at 250° C. At 350° C. an average of about 10% was obtained, but the activity of the walls fluctuated consider-

ably and this value is probably good only to within a factor of 1.5 to 2. At 450° to 500° C. the variations were still more pronounced. The atom concentration was about 2%, but this value is probably uncertain by a factor of 3, and perhaps 4.

Blank Experiments

On account of the small distance between the reaction vessel and the discharge, a very small, but definite amount of methane diffused back into the discharge against the deuterium flow. Inasmuch as a number of previous investigations, and preliminary results in the present work, had all shown that methane is not attacked by deuterium atoms at 20° C., it was possible to use runs at this temperature as blanks to estimate the effect of the penetration of methane into the discharge.

Six experiments of this type under conditions similar to those in the experiments reported indicated that the products of the reaction at 20° C. were 3.0, 4.9, 4.5, 4.7, 5.6, and 4.3% "heavy". The mean, 4.5%, was therefore used as a correction for this factor, and was subtracted from the percentage conversion of CH_4 to CD_4 obtained in the high temperature experiments. This blank value is rather high, but in order to have reduced it, it would have been necessary to increase the D_2/CH_4 ratio to such an extent that very long times, and therefore very large amounts of deuterium, would have been necessary in order to obtain sufficient methane for analysis. (As it was, about 220 cc. of deuterium at N.T.P. were consumed in each experiment.) Actually, however, the blank experiments were very reproducible, and no more uncertainty arises from this cause than is inevitably present on account of the fluctuations in the deuterium atom concentration at high temperatures.

Results

The results of all runs made with the apparatus in its final form are given in Table I.

In arriving at the values tabulated, knowing the rate of flow of deuterium and methane, we first calculate the total volume of gas flowing per second at the temperature and pressure of the reaction vessel. From this and the volume of the reaction vessel we arrive at the reaction time. In performing the calculation it is necessary to correct the gas volume for the expansion due to the splitting of part of the deuterium into atoms.

From a knowledge of the fraction of deuterium present as atoms, and the total pressure, we then get the partial pressure of deuterium atoms in the system and the number of deuterium atoms per cubic centimetre in the reaction vessel. We then calculate $Z_{CH_4.D}$, the number of collisions made by one methane molecule with deuterium atoms in one second. This is obtained from the relation*

$$Z_{CH_4.D} = 2\sqrt{2\pi}\left(\frac{d_D + d_{CH_4}}{2}\right)^2 \sqrt{\frac{M_D + M_{CH_4}}{M_D M_{CH_4}} \cdot RT} \times N_D ,$$

* *See K. F. Herzfeld (11, p. 46) or Bonhoeffer and Harteck (2, p. 183).*

TABLE I

THE REACTION OF DEUTERIUM ATOMS WITH METHANE

Temperature, °C.	Atoms, %	Total flow of gas in cc. per sec. at the temp. and press. of the expt.	Total volume corrected for amount of D_2 present as atoms	Time in reaction vessel, sec.	Partial pressure of D atoms, cm.	N_{D_1} the number of D atoms per cc.	$Z_{CH_4,D}$ per sec.	$Z_{CH_4,D}$ in reaction time	CD_4 in products, (uncorrected), %	CD_4 (corrected), %	Exchange, %	Collision yield	E_1 Kcal. assuming $A = 0.1$	E_1 Kcal. assuming $A = 0.01$
250	20	1043	1153	1.19	5.6×10^{-3}	1.04×10^{15}	5.34×10^{5}	6.35×10^{5}	7.0	2.5	2.8	1.8×10^{-7}	13.7	11.3
250	20	1043	1153	1.19	5.6×10^{-3}	1.04×10^{15}	5.34×10^{5}	6.35×10^{5}	7.4	2.9	3.3	2.0×10^{-7}	13.6	11.2
250	20	1043	1153	1.19	5.6×10^{-3}	1.04×10^{15}	5.34×10^{5}	6.35×10^{5}	6.4	1.9	2.1	1.4×10^{-7}	14.0	11.6
350	10	1243	1308	1.05	2.8×10^{-3}	4.40×10^{14}	2.48×10^{5}	2.61×10^{5}	9.5	5.0	5.6	8.7×10^{-7}	14.4	11.5
350	10	1243	1308	1.05	2.8×10^{-3}	4.40×10^{14}	2.48×10^{5}	2.61×10^{5}	11.3	6.8	7.7	1.2×10^{-6}	14.0	11.2
450	2	1442	1456	0.94	5.6×10^{-4}	7.53×10^{13}	4.55×10^{4}	4.27×10^{4}	14.3	9.8	11.0	1.0×10^{-6}	13.1	9.8
450	2	1442	1456	0.94	5.6×10^{-4}	7.53×10^{13}	4.55×10^{4}	4.27×10^{4}	10.6	6.1	6.9	6.4×10^{-6}	13.8	10.5
450	2	1442	1456	0.94	5.6×10^{-4}	7.53×10^{13}	4.55×10^{4}	4.27×10^{4}	14.7	10.2	11.5	1.1×10^{-6}	13.1	9.8
500	2	1542	1557	0.88	5.6×10^{-4}	7.04×10^{13}	4.41×10^{4}	3.88×10^{4}	11.1	6.6	7.5	7.7×10^{-6}	14.4	11.0
500	2	1542	1557	0.88	5.6×10^{-4}	7.04×10^{13}	4.41×10^{4}	3.88×10^{4}	10.4	5.9	6.7	5.9×10^{-6}	14.8	11.3

Volume of reaction vessel = 1370 cc.; deuterium flow = 0.202 cc. per sec. at N.T.P.; methane flow = 0.0130 cc. per sec. at N.T.P.; pressure = 0.30 mm.

where the d's are the molecular diameters and the M's the molecular weights. Assuming the diameter of the methane molecule to be 3.0×10^{-8} cm., and the collision diameter of a deuterium atom to be the same as that of a hydrogen atom (10), this reduces to

$$Z_{CH_4,D} = 2.25 \times 10^{-11} N_D \sqrt{T},$$

whence we get the values given in Column 8. We then get the number of collisions occurring during the reaction time. The next two columns give the percentage conversion to CD_4, before and after correcting for the blank experiments. From this we get the "percentage exchange" on the assumption that complete exchange would correspond to a uniform distribution of deuterium and hydrogen between methane and hydrogen. The collision yield is then calculated, it being remembered that it takes four fruitful collisions to convert a molecule of CH_4 to CD_4. The back reaction $CD_4+H = CD_3H+D$ has been neglected, since its effect is insignificant for small percentage conversions. The last two columns give the activation energy calculated from the collision yield according to the relation

$$\text{collision yield} = Ae^{-E/RT},$$

the value of E being calculated on the assumption that the steric factor is 0.1 in one case and 0.01 in the other.

Discussion

In Fig. 2 the logarithm of the collision yield is plotted against 1/T. The activation energy calculated from the slope of the full line is 13.5 Kcal. The two dotted lines correspond to 11.5 and 15.3 Kcal. respectively. It is apparent that all that can be said from a consideration of the temperature coefficient is that E is 13.5 ± 2 Kcal.

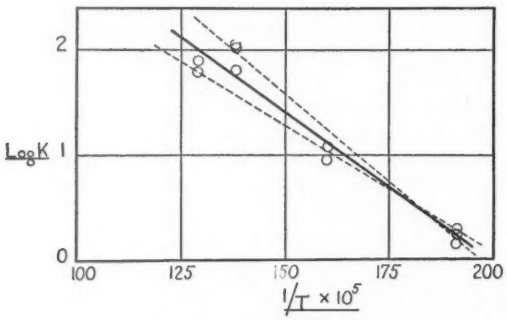

FIG. 2. *The temperature coefficient of the collision yield.*

In Table I the calculated activation energies for each run are shown, the values having been obtained by assuming steric factors of 0.1 and 0.01. The corresponding mean values of E are 13.9 and 10.9 Kcal. respectively. The reaction apparently proceeds in a manner analogous to the reaction

$H_2+D_2 = 2HD$, for which the steric factor is 0.07 (4). Farkas (3) has pointed out that there are grounds for believing that the steric factor in the reaction $D+NH_3$ is only one-quarter as great as this. The methane molecule is more symmetrical than the ammonia molecule, and perhaps the most plausible value for the steric factor is about 0.04. If we assume this we get for E about 12.9 Kcal., which is in complete agreement with that calculated from the temperature coefficient. On account of the fluctuations in the atom concentration and of the relatively large "blanks", the results are only approximate. Making a rather liberal estimate of the probable error, we may state the activation energy to be 12.9 ± 2 Kcal. This is in good agreement with previous estimates, *viz.*

Geib and Steacie (Wood-Bonhoeffer method at low temperatures)	>11 Kcal.
Steacie and Phillips (mercury photosensitization)	11.7
Farkas (Thermal. E not determined but by analogy with the $D+NH_3$ reaction may be estimated as roughly)	11
Farkas and Melville (mercury photosensitization)	13
Morikawa, Benedict, and Taylor (mercury photosensitization)	12.5 to 14
Trenner, Morikawa, and Taylor (Wood-Bonhoeffer method up to 300° C.)	15.6

The results of the present investigation, therefore, although they are only approximate, serve to tie-in the low temperature atomic technique and the high temperature thermal results. The activation energy of the reaction would certainly seem to be established as not far from 12 to 13 Kcal.

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THE ALKALOIDS OF FUMARIACEOUS PLANTS

XV. DICENTRA CHRYSANTHA WALP. AND DICENTRA OCHROLEUCA ENGELM[1]

By Richard H. F. Manske[2]

Abstract

Bicuculline, protopine, and cryptopine have been isolated from both of the species mentioned in the title. In addition, *Dicentra chrysantha* was found to contain two new alkaloids, namely, $-\nu$, $C_{19}H_{17}O_6N$, phenolic, and *chrycentrine*, $C_{18}H_{15}O_5N$, non-phenolic. Neither alkaloid contains methoxyl groups. A very small quantity of a sixth alkaloid, as yet not characterized from *D. chrysantha*, proved to be identical with a base recently isolated from *Corydalis ochotensis*.

Dicentra chrysantha Walp. and *D. ochroleuca* Engelm. are closely related species native to California. In the genus *Dicentra* they are exceptional because of their remarkable upright caulescent habit. Of the species that have been chemically examined only the Asiatic *D. spectabilis* has a stem. All others are stemless and this distinctive habit is reflected not only in the large number of contained alkaloids but in their character. *D. cucullaria* is the only species of the stemless group that thus far has not yielded an alkaloid of the aporphine type.

Owing to the relative inaccessibility of the plants under discussion, it has not been possible to carry their investigation as far as is desirable. In view of the fact, however, that more material will not be immediately available, it seemed expedient to publish the present observations.

Six alkaloids have been isolated from *D. chrysantha* and of these, bicuculline, protopine, and cryptopine are already known. A fourth alkaloid proved to be identical with one recently isolated from *C. ochotensis*, and its further characterization is reserved for a publication dealing with that plant. A small amount of the alkaloid ($-\nu$), giving analytical figures in agreement with $C_{19}H_{17}O_6N$, was present. It appears to be phenolic and probably lactonic. Methoxyl is absent, although an N-methyl group is present. The sixth alkaloid, for which the name *chrycentrine* is now proposed, also appears to be new. It is non-phenolic and probably contains two methylene-dioxy groups, but methoxyl groups are absent. Its empirical formula, $C_{18}H_{15}O_5N$, probably relegates it to the rapidly increasing group of Fumariaceous alkaloids containing five oxygen atoms. Three members of this series, which evidently does not include the structural features of the protopine group, were recorded in a communication dealing with *Corydalis sibirica* (3).

In the case of *D. ochroleuca*, there was available only one kilo of dried material, and the difficulty of a thorough examination was enhanced by the very low content of total alkaloids. Although indications of the presence

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of other alkaloids are not lacking, bicuculline, protopine, and cryptopine are the only ones obtained in a state of purity.

It is relevant finally to mention an examination of *D. spectabilis* with the object in view of securing for identification the alkaloid melting at 142° C., which Danckwortt (1) isolated from this source. No alkaloid other than protopine could be isolated from 3.2 kilos of dried material of which the roots constituted 1.2 kilos. All fractions were carefully examined and the ultimate uncrystallized residue weighed only a few milligrams. Fumaric acid was particularly abundant in the aerial portion and its presence in *D. chrysantha* and *D. ochroleuca* was readily demonstrated.

Experimental

The procedure repeatedly employed by the author, and first detailed in the case of *Adlumia fungosa* (2), was used for separating the total alkaloids into a number of fractions. It may be added here that chloroform extraction of the aqueous acid solution (*S*) is most conveniently accomplished when it is not too dilute. A convenient concentration is such that a litre of solution is prepared from each kilo of plant material. In most cases separation of the two liquid phases is rapid and well defined, although the first addition of the chloroform generally causes the separation of a resinous product soluble in neither medium. When the amount is small its presence may be disregarded since it adheres to the walls of the separatory funnel. Larger quantities are desirably removed by filtration.

There was available six kilos of dried *D. chrysantha*, of which the roots constituted 1.5 kilos. The total dry material of *D. ochroleuca* weighed one kilo. The author is greatly indebted to Dr. Carl B. Wolf, Director of the Santa Ana Botanical Gardens, Anaheim, California, through whose kindness these materials were made available.

Isolation of Bicuculline from D. chrysantha

The amorphous dark fraction (*BC*) was dissolved in hot methanol and the filtered solution (charcoal) evaporated to a thin syrup. In the course of several days a small crystal nucleus had appeared, and when this was broken up with a rod rapid crystallization ensued. After filtering and washing, this alkaloid melted indefinitely at 185° C.* After one recrystallization from chloroform-methanol it melted at 194° C. A mixture of the product with the high melting form of bicuculline (m.p. 196° C.) melted at 195° C. The identity with bicuculline was further established by solution in hot chloroform, evaporation to a syrup, and addition of hot methanol, together with a nucleus of bicuculline (m.p. 177° C.). Crystallization was immediate and the bicuculline then melted at 177° C., either alone or in admixture with an authentic specimen. The yield was 1.9 gm. (0.03%).

In the case of *D. ochroleuca* the crude bicuculline melted at 175° to 177° C. solidified on further heating, and remelted at 193° C. After one recrystalliza-

* *All melting points are corrected.*

tion as above, it melted sharply at 177° C., and this melting point was not depressed when the alkaloid was admixed with an authentic specimen of bicuculline. The yield was 0.05%.

Isolation of Chrycentrine

The filtrate from the crude bicuculline was acidified with hydrochloric acid, water added, and the methanol boiled off. The filtered aqueous solution was basified with ammonia and the liberated base extracted with much ether. An insoluble resin separated on the walls of the separatory funnel. It was separately recovered by extraction with chloroform. During the evaporation of the ether extract to a small volume a sparingly soluble base crystallized. It was dissolved in hot chloroform in which it is sparingly soluble, and the solution was evaporated to a small volume. The addition of methanol yielded colorless stout prisms which melt at 216° C. Concentrated sulphuric acid dissolves this alkaloid to form a pale yellow solution, which on warming changed to brown, then to pink and on further heating to olive. With 80% sulphuric acid and phloroglucinol at 100° C., it yielded a red precipitate characteristic of the methylene-dioxy group. The yield of *chrycentrine* was about 0.01 gm., which included a small amount of the same alkaloid obtained from the chloroform extract of the ether-insoluble resin. Calcd. for $C_{18}H_{15}O_5N$: C, 66.48; H, 4.62; N, 4.31%. Found: C, 65.33; H, 4.75; N, 4.16% (means of duplicates).

The mother liquors from the crystallization of the chrycentrine were combined and redissolved in dilute hydrochloric acid. The bases were regenerated by adding excess potassium hydroxide and extracting with ether. The residue from the extract, in contact with a little methanol, deposited a small amount of crystalline material. This melted indefinitely at 220° C. When recrystallized from chloroform-methanol it was obtained in colorless stout prisms, which melted at 223° C. In appearance, solubility, and melting point this base is identical with an alkaloid isolated in relatively larger quantity from *Corydalis ochotensis*, and admixture of the two caused no depression in melting point.

Isolation of Alkaloid-v

The ether extract representing fraction (*EC*) was freed of solvent, dried, and moistened with methanol. The crude crystalline material thus obtained melted at about 220° C. It was recrystallized from chloroform-methanol, and it then consisted of well formed stout prisms melting at 230° C. Calcd. for $C_{19}H_{17}O_6N$; C, 64.23; H, 4.79; N, 3.94%. Found: C, 65.25; H, 4.62; N, 4.01%.

Isolation of Protopine and Cryptopine

The isolation of protopine from fraction (*BS*) and as a contaminant from (*ES*) has been repeatedly described. In the case of *D. chrysantha* the yield was 0.17%, and in the case of *D. ochroleuca* it was 0.22%. The methanolic mother liquors from both sources were largely freed of solvent and rendered just acid by the addition of hydrobromic acid. During the course of several

days the characteristic pearly lustrous plates of cryptopine hydrobromide separated from both solutions. Regeneration of the free bases and recrystallization from chloroform-methanol yielded pure cryptopine which in each case melted at 221° C., and admixture with authentic cryptopine did not lower these melting points.

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